Improving the competitiveness of the electrolytic zinc process by chemical reaction engineering approach

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PREFACE

The experimental work and industrial applications described in this thesis were carried out mainly during two periods, from 1968 to 1975, and 1990 to 1999 at Outokumpu Oy. The broadening of the scientific background, through kinetic and thermodynamic modeling of the most important and chemically interesting processes, has been performed at Åbo Akademi starting from 2006.

I wish to express my warmest thanks to all my colleagues within research, operation and engineering at Outokumpu Oy for their excellent cooperation and the inspiring attitude towards new developments. Implementation of the processes in practice was of course what boosted the value of this development work, and the readiness of the people responsible for the production to be the first ones to go for new technology was really inspiring and is greatly appreciated.

I am very grateful also to Outotec Oyj and Mikko Ruonala for giving the permission to publish this material.

I express a special thanks to Professor Jussi Rastas for his invaluable support and inspiration in my first job within the hydrometallurgical field.

All my colleagues at Åbo Akademi University have my deepest gratitude for all the support and help I have readily got whenever it has been needed – and it has! I appreciate highly the advice and assistance I have got from Professor Tapio Salmi, and Professor Dmitry Yu. Murzin. Tapio´s advice concerning writing: - "just tell the story" - has been a highly appreciated guideline to follow. During my work on modeling Dmitry gave the advice to look at use of the semi-empirical Avrami's equation. This has in my opinion shown to be a good and simple modeling tool to use both for leaching and precipitation in this work.

I wish to thank Professor Johan Wärnå for his assistance in the kinetic modeling and him and Dr Kari Eränen for their assistance in all practical issues and Dr Pasi Tolvanen for his invaluable help with finalizing the manuscript. To my room-mate during all this year's Dr. Narendra Kumar I wish to extend my warmest thanks for guidance in the English language and discussions on items like research philosophy on high levels. Any new, practical outcome has probably been meager, as we have always been of the same opinion.

Finally, special tanks to my wife Ritva and my whole family and Nana for their patience and support.

Åbo, February 2014

Sigmund Fugleberg

ABSTRACT

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Improving the competitiveness of the electrolytic zinc process by chemical reaction engineering approach

Doctoral thesis, Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Department of Chemical Engineering, Åbo Akademi University, 2013

Keywords: Electrolytic zinc process, process development, leaching, solution purification, jarosite precipitation, copper removal, cobalt removal, cadmium removal, fluidized bed, atmospheric leaching of concentrate

This doctoral thesis describes the development work performed on the leach- and purification sections in the electrolytic zinc plant in Kokkola to increase the efficiency in these two stages, and thus the competitiveness of the plant. Since metallic zinc is a typical bulk product, the improvement of the competitiveness of a plant was mostly an issue of decreasing unit costs.

The problems in the leaching were low recovery of valuable metals from raw materials, and that the available technology offered complicated and expensive processes to overcome this problem.

In the purification, the main problem was consumption of zinc powder - up to four to six times the stoichiometric demand. This reduced the capacity of the plant as this zinc is re-circulated through the electrolysis, which is the absolute bottleneck in a zinc plant. Low selectivity gave low-grade and low-value precipitates for further processing to metallic copper, cadmium, cobalt and nickel. Knowledge of the underlying chemistry was poor and process interruptions causing losses of zinc production were frequent.

Studies on leaching comprised the kinetics of ferrite leaching and jarosite precipitation, as well as the stability of jarosite in acidic plant solutions. A breakthrough came with the finding that jarosite could precipitate under conditions where ferrite would leach satisfactorily. Based on this discovery, a one-step process for the treatment of ferrite was developed. In the plant, the

new process almost doubled the recovery of zinc from ferrite in the same equipment as the two-step jarosite process was operated in at that time. In a later expansion of the plant, investment savings were substantial compared to other technologies available.

In the solution purification, the key finding was that Co, Ni, and Cu formed specific arsenides in the “hot arsenic zinc dust” step. This was utilized for the development of a three-step purification stage based on fluidized bed technology in all three steps, i.e. removal of Cu, Co and Cd. Both precipitation rates and selectivity increased, which strongly decreased the zinc powder consumption through a substantially suppressed hydrogen gas evolution. Better selectivity improved the value of the precipitates: cadmium, which caused environmental problems in the copper smelter, was reduced from 1-3% reported normally down to 0.05 %, and a cobalt cake with 15 % Co was easily produced in laboratory experiments in the cobalt removal. The zinc powder consumption in the plant for a solution containing Cu, Co, Ni and Cd (1000, 25, 30 and 350 mg/l, respectively), was around 1.8 g/l; i.e. only 1.4 times the stoichiometric demand – or, about 60% saving in powder consumption.

Two processes for direct leaching of the concentrate under atmospheric conditions were developed, one of which was implemented in the Kokkola zinc plant. Compared to the existing pressure leach technology, savings were obtained mostly in investment

The scientific basis for the most important processes and process improvements is given in the doctoral thesis. This includes mathematical modeling and thermodynamic evaluation of experimental results and hypotheses developed.

Five of the processes developed in this research and development program were implemented in the plant and are still operated. Even though these processes were developed with the focus on the plant in Kokkola, they can also be implemented at low cost in most of the zinc plants globally, and have thus a great significance in the development of the electrolytic zinc process in general.

REFERAT

Sigmund Fugleberg

Förbättring av den elektrolytiska zinkprocessens konkurrensförmåga med processtekniska metoder

Doktorsavhandling, Laboratoriet for teknisk kemi och reaktionsteknik, Prosesskemiska centret, Institutionen för kemiteknik, Åbo Akademi, 2013

Nyckelord: electrolytisk zinkprosess, processutveckling, lakning, lösningsrening, jarositutfällning, kopparavlägsning, koboltavlägsning, kadmiumavlägsning, fluidiseradd bädd, atmosfärisk lakning av koncentrat

I denna doktorsavhandling beskrivs utvecklingsarbeten som utförts inom laknings- och lösningsreningsavdelningarna vid den elektrolytiska zinkfabriken i Karleby för att öka effektiviteten av dessa två avdelningar, och därmed förbättra fabrikens konkurrensförmåga. Metallisk zink är en typisk bulkprodukt och därför var förbättringen av konkurrensförmågan närmast en fråga om att reducera enhetskostnader.

Problemen i lakningen var ett lågt utbyte av värdefulla metaller från råmaterialen, och att tillgänlig teknologi för att förbättra utbyten var tekniskt komplicerad och dyr.

I lösningsreningen var det största problemet ett fyra till sex gånger högre förbruk av zinkpulver jämfört med det stökiometriska. Detta reducerade fabrikens kapacitet då denna zinkmängd cirkulerar via elektrolyssteget, som alltid är den absoluta flaskhalsen i produktionslinjen. Svag selektivitet gav låggradiga Cu-, Cd- och Co/Ni-fällningar med ett lågt värde med tanke på en vidareförädling till metaller. Kännedomen om processens kemi var bristfällig, vilket förorsakade produktionsbortfall genom upprepade prosesstörningar.

Studier av lakningen omfattade kinetik vid lakning av ferrit, utfällning av jarosit samt stabilitet av jarosit i processlösningar. Ett genombrott gjordes då man upptäckte att jarosit kunde falla ut under förhållanden, där också ferrit urlakades med en acceptabel hastighet. På basis av detta utvecklades en enstegsprocess för behandling av ferrit. Då denna process, i samma anläggning, ersatte den existerande tvåstegsjarositprocessen, erhölls ett ungefär fördubblat utbyte på

zink från ferriten. I den senare expansionen av fabrikens kapacitet erhölls betydande inbesparningar i investeringarna jämfört med konkurrerande, tillbudsstående teknologi.

Den centrala upptäckten inom lösningsreningen var att kobolt, nickel och koppar föll ut som specifika arsenider i "hot arsenic zinc dust" koboltavlägsningssteget. Detta var utgångspunkten för utveckling av en trestegsreningsprocess, d.v.s. avlägsning av koppar, kobolt och kadmium, där alla tre stegen baserades på fluidiseradbäddteknologi. Både utfällningshastigheter och -selektiviteter förbättrades och förbrukningen av zinkpulver minskade avsevärt genom att vätgasutvecklingen kunde undertryckas. Den förhöjda selektiviteten förbättrade värdet av fällningarna. Kadmiumhalten som förorsakade miljöproblem vid kopparsmältverket minskades från 1-3% till 0.05%. Från en lösning med 20 mg/l Co vore det möjligt att producera en fällning med 10-15 % Co. Förbrukningen av zinkpulver för en lösning med 1000 mg/l Cu, 25 mg/l Co, 30 mg/l Ni och 350 mg/l Cd låg normalt på ca 1.8 g/l eller bara 1.4 gånger den teoretiska.

Studier på direkt lakning av koncentrat vid atmosfäriskt tryck resulterade i två processalternativ, av vilka den ena processen togs i användning i Karleby.

Doktorsavhandlingen ger en vetenskaplig bakgrund för de viktigaste processerna och processförbättringarna. Detta arbete omfattar matematisk modellering och thermodynamisk evaluering av erhållna experimentella resultat och uppställda hypoteser.

Fem av processerna som utvecklades inom detta forsknings- och utvecklingsprogram implementerades i Karlebyfabriken, där de fortfarande är i användning. Trots att dessa processkoncept utvecklades med tanke på just denna fabrik, kan de med små kostnader implementeras i de flesta zinkfabriker överallt i världen och arbetet är därför av generell betydelse för utveckling av elektrolytisk zinkframställning i almänhet.

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CONTENTS

Appendix

1 INTRODUCTION

1.1 Zinc - occurrence, raw materials, properties, and economic importance

The chemical sign for zinc is Zn and its average occurrence in Earths crust is about 0.01%. It is present in many minerals, but regarding its industrial production, the sulfide, sphalerite, (Zn,Fe)S, and its degradation products, carbonate and silicate, are the only major raw materials. The best ores can contain from 10 to 20% Zn, but even much lower grades are mined.

Zn has a melting point of 419.5 °C boiling point 907 °C and density 7.14 g/cm^3. With a standard electrode potential of -0.762 V, it is very reactive and should be oxidized by water under hydrogen evolution. This reaction has, however, a very high overpotential and zinc can even be electrodeposited from strongly acidic solutions.

Zinc immediately oxidizes in air, but the oxide layer formed will soon render it passive at ambient atmosphere, and further oxidation is therefore extremely slow. This passivation, the low melting point and is ability to adhere strongly to the surface of steel makes it an excellent corrosion coating, and this field stands also for its major use, in fact about 50% of the world production. Other major uses are in brass, die cast as well as other alloys and chemicals.

Zinc is also very important for human health. The human body contains 2 to 3 g of zinc (iron about 6 to 8 g) and the recommended daily intake is 10 to 15 mg. It is important for the function of more than 300 enzymes in the human body, and deficiency can lead to neuropsychological disturbances, growth retardation, dermatitis, lethargy, and loss of appetite and hair.

World annual production was 2011 about 13 Mt at a value of about 30 billion $/a. This represented worldwide about 1.5 kg/a, or 4 $/a per capita. The corresponding figures for Finland were about 0.3 Mt/a, 0.6 to 0.9 billion $/a, 60 kg/a worth about 120 $/a per capita. The zinc industry is thus significantly more important for Finland than it is worldwide.

Most of the primary zinc in the world is produced from sulfide concentrates, which typically contain from 50 to 55% Zn and 30 to 33% S, whereas the rest of the concentrate comprises a variety of elements, with Fe, typically 5 to 10%, as the major one. A second important raw material base is oxidized, secondary ores, composed of carbonates and silicates.

Besides Zn, the concentrates contain varying quantities of minor elements, Cu, Cd, Pb, Ag, Au, In, Ga, Ge, Co, Ni, Hg and Se with potential economic value [1 - 4].

1. 2. Outline of zinc production methods.

Until about 1920, zinc was only produced pyrometallurgically. In these processes, sulfur in the concentrate is first removed as SO_2 gas by roasting with air, which leaves the metals in oxide form. The oxides are then mixed with coke and heated to about 1100 °C where Zn oxide is reduced to the metallic state and evaporates. Zn vapor is condensed, and the impurities, mainly Pb and Cd, are separated from zinc through fractional distillation.

Electrolytic production of Zn from aqueous solutions, which is the subject of this work, had been under development already from around 1860, but commercially operating plants were built first during and after the World War I. Today, the electrolytic zinc process is the dominating one and accounts for more than 90% of the global production, while the pyrometallurgical processes are still losing their share.

The electrolytic zinc process, a principal flowsheet is shown in Fig.1, consists principally of four major stages where impurity elements are removed. The first step is roasting of the sulfide concentrate to produce acid soluble metal oxides, calcine, and remove SO_2 gas which is further processed to H_2SO_4.

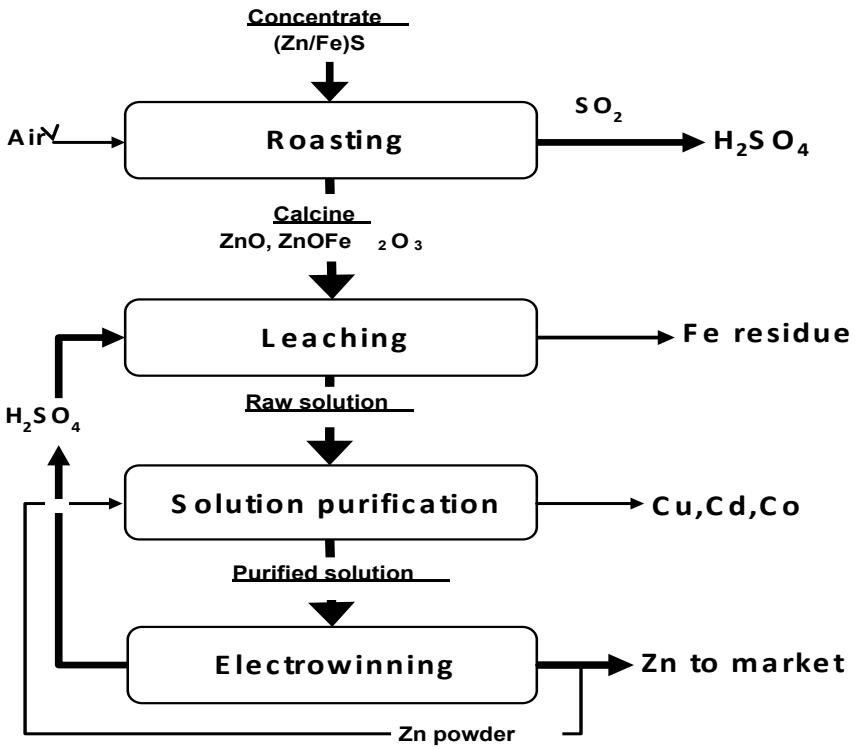

Fig 1. Principle flowsheet of the electrolytic zinc process.

The oxide material from the roasting, calcine, where the major Zn compounds are zinc oxide, ZnO, and zinc ferrite, $ZnOFe_2O_3$, is leached in a H_2SO_4 solution. The leaching produces a neutral $ZnSO_4$ solution, raw solution, and the iron is rejected as a solid residue.

The impure Zn sulfate solution is purified from certain detrimental trace elements by cementation with Zn powder, and the pure solution is sent to the electrowinning step, where Zn is deposited on Al cathode sheets, and H_2SO_4 is regenerated at the anode. The acid solution," spent acid," is recycled to the leaching step. Thus the reagent, the H_2SO_4, is in a closed loop in the process. Powder is produced from part of the zinc and returned as reagent in the solution purification. Rest of the zinc is marketed.

The concentration of the circulating solution is determined by the solubility of the metal sulfates, which means a maximum SO_4^{2-} content of 400 to 450 g/l to maintain a sufficient margin from the crystallization point of any of the contained metal sulfates. Dependent on the concentration of other metals than zinc in solution, mainly Mn and Mg, which are accumulated in the circuit, the feed to the electrolysis contains 150 to 190 g/l of Zn. The return acid from the electrolysis contains typically 150 to 190 g/l of H_2SO_4 and around 50 g/l of Zn [4].

1. 3 Aspects on electrolytic production of zinc

The composition of a concentrate from a single mine remains normally fairly constant over its whole life time, but, between mines, the variations can be substantial, - especially concerning minor elements. Of these, Hg and Se are removed during roasting and eventually recovered and refined to marketable products. The rest of the elements mentioned above go to the calcine. Variations in the composition of calcine which can be obtained from different concentrates are shown in Table 1.

In most zinc plants which buy concentrates from a number of mines, so-called custom smelters, the composition of the feedstock can vary significantly. Even though zinc represents by far the major economic value of an average concentrate, the metal value of minor elements can in some cases be significant. Variations in metal contents and potential values of the minor metals in the calcines are indicated in Table 1. Both contents and product prices are roughly estimated since both vary considerably.

The values are given both in per ton of concentrate and in metal values for a medium-size plant producing 200 000 t of Zn per year.

No plant has a feed with even close to the maximum content of all the valuable minor metals shown in Table 1, and thus the main objective in most plants is to

optimize the production line with focus on zinc, i.e. to achieve a maximum recovery of zinc at the lowest possible operating and investment costs.

Table 1. Variation of element composition and metal values in zinc concentrates obtained from different concentrates [5].

	Element	Content	Price	Metal value		
		%, g/t	$/t or $/g	$/t conc.	M$/200 kt Zn	% of Zn
Elements recovered	Zn	50 - 60	2000	1000 - 1200	350	100
	Cu	0.1 - 2	8000	8 - 160	2.5 - 50	0.7 - 14
	Cd	0,1 - 0.5				
Occasionally recovered	Pb	0.2 - 2	2000	4 - 40	0.7 - 7	0.3 - 3
	Ag	10 - 300	0.5	5 - 150	0.8 - 42	1 - 10
	Au	0 - 2	60	0 - 160	0 - 8	0 - 2
Elements seldom recovered	Co	5 - 100	0.03	0.1 - 3	0 - 4	0 - 2
	Ni	5 - 100	0.01	0.05 - 1	0 - 0.5	0 - 0.2
	Ge	5 - 100	1	5 - 50	1 - 42	0.5 - 10
	Ga	1 -100	0.5	0.5 - 50	0.4 -40	
	In	1 -100	0.2	0.2 - 40	0.1 - 16	
Elements sent to waste	Fe	2 - 12				
	Al	0.1				
	SiO_2	0.5 - 2				
	Mg	0.01- 0.2				
	Mn	0.01 - 0.5				
	S	2				

With the normally low total value, an eventual recovery of minor elements should not cause any additional costs to the Zn production line, which implies that they should be taken out from the process as high-grade by-products suitable for easy upgrading to marketable products.

Traditionally the most valuable minor metals have been Pb and Ag.

Fe, Al, Mg, Mn, As and SiO_2 in the calcine have no commercial value, but they induce a considerable cost, partly from their separation operations and partly by causing losses of the valuable elements with the residues they form.

1.4. General description of the electrolytic zinc process

Until about 1970, operating plants had normally a two-step countercurrent, leaching, also referred to as “neutral leaching”, leading to a final pH of about 4.8 - 5. Under these conditions only Zn in the oxide is leached. The ferrites, together with other insoluble compounds and the valuable elements Pb, Ag, Au, Ge, Ga, and In end up in the leach residue, which at many plants were stockpiled. The losses with this ferrite residue were considerable, and the

recoveries from a calcine containing 10% Fe remained o on an average at only 88 to 90% for Zn, respective 50 and 60% for Cu and Cd.

During the 1960´s, processes for hydrometallurgical treatment of the ferrite had been developed on laboratory and pilot plant scales in Norway, Spain, Australia, Belgium and Japan. In these processes, the ferrite was leached, and the iron, which also was dissolved, was re-precipitated as rather Zn-free, crystalline compounds with reasonable filterability. These compounds were sodium or ammonium jarosite $A[Fe_3(SO_4)_2(OH)_6]$, [6], goethite FeOOH, [7], and hematite, Fe_2O_3 [8]. Hydrometallurgical treatment of ferrite had earlier been hindered by difficulties to precipitate iron compounds with good filtering properties. These new processes would raise recovery of Zn, and incorporation of these processes into both new and old plants were in the planning stage.

The electrode potential of zinc, E_0 = -0.763 V, means that thermodynamically Zn should not be electrodeposited from an acidic aqueous solution, but H_2 gas evolution should be the result. The H_2 gas formation on metallic Zn is, however, very strongly hindered and the overpotential needed to affect the H_2 formation is under favorable conditions higher than 0.763 V. This makes the practical nobility of Zn higher than that of H_2, and thus Zn can be electroplated from solutions containing even 200 g/l H_2SO_4 with a current efficiency of above 90%.[9] This allows for regeneration of a suitable acid solution for the leaching operation and a closed solution circuit. The H_2 formation is very sensitive to certain elements more noble than Zn. These will co-precipitate during electrolysis and provide sites with much lower overpotential for H_2 gas evolution than on the pure Zn surface. These impurities; especially Sb, Ge and As, cause a considerable increase in H_2 gas evolution, and even concentrations as low as 50 to 100 µg/l can completely bar the deposition of Zn. A very thorough removal of all detrimental impurities before the electrowinning step is consequently of outmost importance. Ineffective purification techniques had also been the most important reason for the 50 - 60 years that had been needed to develop an industrially working process.

Removal of Co and Ni, though nobler than Cd do not precipitate with Zn powder only, but require some additional reagents, of which As^{3+} and Sb^{3+} salts like As_2O_3 and K-Sb-tartrate were used. These additional reagents were referred to as “activators” [10].

1.4.1. Stand of the chemistry in the leaching in 1970

1.4.1.1. *Neutral leach*

The primary objective of the neutral leaching, (NL), is to extract maximum amount Zn from the zinc oxide, ZnO, into a concentrated $ZnSO_4$ solution with the lowest possible impurity level. High extraction of Zn is favored at low pH, while the purity of the final solution, "neutral solution", by a higher pH to precipitate impurities with less soluble hydroxides than $Zn(OH)_2$. To fulfill these two conflicting objectives, the leach of the oxide is normally divided into two counter-currently operated steps illustrated in Fig 2.

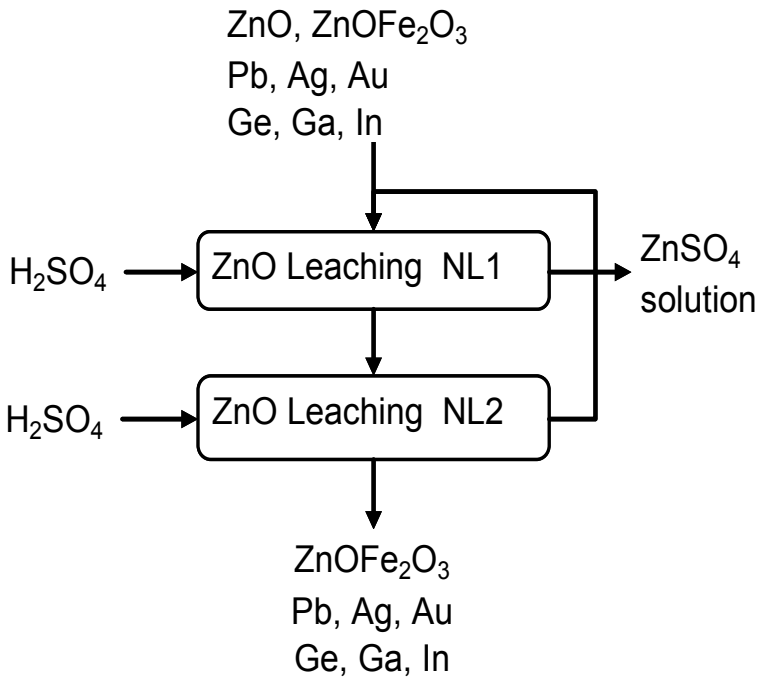

Fig. 2 Principle of a normal neutral leach step.

The first step, NL1, is operated to give a final pH of about 5 (at room temperature), - or the highest pH, at which precipitation of basic zinc sulfates is avoided. To obtain a reasonable reaction time, the presence of a substantial excess ZnO is necessary in this step. In the second step, NL2, to which the solid from NL1 is directed, the leaching is continued at a lower pH, normally about 1.5, at which the excess ZnO can be leached. At this low pH impurities such as Al, As, Sb, Ge, Ga, In, and even Fe^{3+} have considerable solubilities, but they are re-precipitated when the solution is returned to the NL1 step. This

causes an internal circulation of these elements, which ends when their concentrations in the NL2 step are exceeding their solubility limits. Thus the major part of the mentioned elements has their final out-let from the acidic NL2 step. Before 1970, the leaching process comprised only these two steps.

Only ZnO is leached in the NL1 step, mostly by the added acid according to the reaction:

$$ZnO + H_2SO_4^{2-} => ZnSO_4 + H_2O \quad (1)$$

and partly by the re-precipitation of the recycled elements such as Fe^{3+}, Al, As, Sb, Ga, In, as hydroxides or salts:

$$3ZnO + Fe_2(SO_4)_3 + 3H_2O => 2Fe(OH)_3 + 3ZnSO_4 \quad (2)$$

$$3ZnO + 2H_3AsO_4 + Fe_2(SO_4)_3 => 2FeAsO_4 + 3ZnSO_4 + 3H_2O \quad (3)$$

Precipitation of ferric hydroxide from the recycled solution in NL1 will very easily give an amorphous, slimy precipitate, which is upsetting the solid-liquid separation. Consequently, the quantity of Fe^{3+} returned with the NL2 solution has to be limited. In this simple two-step process, the acid concentration was kept low to leach only ZnO, whereas $ZnOFe_2O_3$ and most of the remaining valuable elements were left in a combined solid residue. The loss of Zn with this residue would normally vary between 5 to 12%, dependent on the iron content of the concentrates.

Other metals, Cu, Cd, Co, Ni and Tl, which are partly leached, have higher solubilities of their hydroxides than $Zn(OH)_2$, thus staying in the $ZnSO_4$ solution. These metals are removed in the succeeding solution purification stage.

Pb and Ag stay in the residue as $PbSO_4$ and respectively Ag_2S and AgCl.

1.4.1.2. Treatment of ferrite

Leaching of $ZnOFe_2O_3$ with acid had long been known, but the recovery of Zn from the resulting solution had been hindered by the difficulties in producing filterable compounds in the re-precipitation of Fe. The crystalline structure of the iron compounds, ie. jarosite, $*)A[Fe_3(SO_4)_2(OH)_6]$, goethite FeOOH, and hematite, Fe_2O_3 in the three new processes for ferrite treatment solved this problem [6, 7, 8] (*): A can be Na, NH_4, Pb, Ag, Tl). The major differences between the processes, which were named according to the precipitated iron compounds, are mostly laying in different treatment of the iron containing solution.

Leaching of ferrite was performed with the spent acid from the electrolysis at H_2SO_4 concentrations exceeding 30 g/l

$$ZnOFe_2O_3 + 4H_2SO_4 \Rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad (4)$$

This leach produced a solution with typically 25 to 30 g/l Fe^{3+} and 30 g/l H_2SO_4.

In the Hematite and Goethite processes the ferric iron in the leach solution is reduced to the ferrous state by concentrate, which produces elemental sulfur, or by SO_2 gas:

$$Fe_2(SO_4)_3 + ZnS \Rightarrow 2FeSO_4 + ZnSO_4 + S \quad (5a)$$

or

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O \Rightarrow 2FeSO_4 + 2H_2SO_4 \quad (5b)$$

In the Hematite Process, iron is re-oxidized and precipitated in autoclaves at 180 to 200 °C:

$$2FeSO_4 + 0.5O_2 + 2H_2O \Rightarrow Fe_2O_3 + 2H_2SO_4 \quad (6)$$

At this temperature hematite is stable at such high acidities that the precipitation can be performed without neutralization of the liberated acid. With an initial Fe^{2+} concentration of 25 to 30 g/l in the feed solution, final acid concentration reaches 50 to 60 g/l H_2SO_4.

Goethite was precipitated from the ferrous iron solution by oxidation at a pH of 3 to 4:

$$6FeSO_4 + 1.5O_2 + 6ZnO + 3H_2O \Rightarrow 6FeOOH + 6ZnSO_4 \quad (7)$$

The precipitation rate is here controlled by the oxidation rate. This gives improved and more stable filtering properties of the precipitate as it provides a low and constant Fe^{3+} concentration throughout the whole precipitation cycle. This is more difficult to attain in precipitation from ferric iron solutions, where the rate is controlled by the addition of solid ZnO. With the high pH needed in the precipitation all liberated acid has to be neutralized by ZnO. The ZnO has normally to be provided by calcine, which usually is the only reagent available in commercially and chemically sufficient quantities.

In the Jarosite process the precipitation is performed with the iron in ferric state at a pH of about 1.3 in presence of certain ions, which for economical reasons were limited to Na^+ and NH_4^+:

$$3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 6ZnO + 6H_2O \Rightarrow 2NH_4[Fe_3(SO_4)_2(OH)_6] + 6ZnSO_4 \quad (8)$$

Also at this pH, neutralizing of most of the liberated acid is necessary, but not as complete as in the Goethite process.

In the Hematite process the overall recovery of Zn from the ferrite is determined almost entirely by the small losses in the ferrite leach stage. In the Goethite and Jarosite processes, Zn is also lost with the ferrite in the neutralizing calcine, as this is not leached at the prevailing pH in the precipitation step.

From the iron precipitation steps, the solution is returned to the neutral leach, and its ferric iron content has to be sufficiently low to avoid disturbances caused by precipitation of amorphous ferric hydroxides.

1.4.1.3 Behavior of valuable minor elements in the jarosite process

In the leaching of zinc ferrite, $ZnOFe_2O_3$, the extraction of most detrimental elements is increased. Therefore, since iron is removed in the jarosite step at a lower pH than in a normal NL2 step, an increased internal circulation of some elements would likely occur.

Pb, Ag and Au stay as solids even at the higher acid concentration in the leaching, Pb as $PbSO_4$ and Ag mostly as Ag_2Cl_2. The solution normally contains 100 to 200 mg/l Cl^-, which re-precipitates any dissolved Ag. Dutrizac has found that 25 mg/l of Cl^- reduces the concentration of Ag to less than 0.1 mg/l, which is less than 0.5 g Ag per ton of Zn concentrate [11]. Au occurs probably in the elemental state. Extraction of Cu, Cd, Co and Ni will increase - and as well will the demand on the purification steps.

Indium and gallium appear always in the trivalent state and their chemical behavior is very close to that of ferric iron. Both are dissolved at a high degree of extraction in the acid leach, but are re-precipitated together with the iron, both as hydroxide and jarosite.

Available solubility products of some basic compounds: $In(OH)_3$ $3.6*10^{-38}$, $Ga(OH)_3$ $1.1*10^{-30}$, GaOOH $3.1*10^{-40}$, $Fe(OH)_3$ $3.4*10^{-38}$, $Al(OH)_3$ $2.7*10^{-31}$ show that at the end of the neutral leach, where Al in solution is normally less than 5 mg/l, In and Ga should be completely removed from the solution. The work by Dutrizac [12] on co-precipitation with jarosite has shown that both elements form practically ideal solid solutions with iron in jarosite and are removed in the same proportion as iron.

Germanium does not form any jarosite type of precipitate, but it is known to precipitate with $Fe(OH)_3$ at the end of the neutral leach. This has mostly been described as an adsorption process. As Ge does not precipitate with jarosite, a considerable internal circulation of Ge takes place between the jarosite stage

and the neutral leach. This results in very high Ge concentrations in the return solution to the neutral leach.

1.4.2. Stand of the chemistry in the purification in 1970

Impurities detrimental for the electrolysis, such as Cu, Cd, Co, Ni, Pb, Tl, As, Sb and Ge, are removed in this step. These elements are all more electropositive than Zn, and will be reduced in the electrolysis together with zinc at the cathode. Of these elements, Cu, Cd, Pb and Tl will be deposited and cause contamination of the zinc product. The other elements will not to any higher extent be found in the zinc; however, they will strongly activate the formation of H_2 gas on the cathode by lower the overpotential of H_2 gas evolution. Sb, Ge and As are especially detrimental, and concentrations of only 0.1 mg/l of Sb can cause merely H_2 gas to be produced at the cathode. This is causes serious damage through loss of Zn production.

With these impurities being nobler than Zn, the predominant technology for removal has been cementation with Zn powder to obtain a metallic precipitate:

$$Me^{n+} + n/2Zn = Me + n/2Zn^{2+} \quad (9)$$

This reaction works well for Cu, which has a positive standard potential, but, in cementation of elements having a negative potential, re-dissolution of metals under formation of hydrogen will be a competing reaction:

$$Co + 2H^{+} = Co^{2+} + H_2 \quad (10)$$

This can be a dominating reaction and hinder the precipitation of the metals almost completely. It can also cause re-dissolution of primarily precipitated metals. Especially Co has been found to be very difficult to remove with Zn powder alone, and a number of different additives had been screened to enhance the precipitation. Of these additives As and Sb salts like As_2O_3 and K-Sb-tartrate, turned out to be the most effective ones, and their applications had been divided almost equally between plants. Co-specific reagents like α-nitroso-β-naphthol had also been used.

In 1917, a method for Co removal, using addition of sodium arsenite in the presence of Cu^{2+} and Zn dust was patented by Electrolytic Zinc Company of Australasia, where it, however, was never applied [13]. This method became, however, popular elsewhere and was a widely used method for Co removal worldwide in 1970, and it was also adopted for the plant at Kokkola. At that time, the knowledge about the mechanisms of this purification system was very poor and the operational practice, which was based more on the experience at individual plants than on well-understood chemistry, varied from plant to plant.

The compound Co formed had not been identified and As was referred to as an "activator". It was also generally regarded that a high concentration (400 - 500 mg/l) of Cu^{2+} was needed, as well as a temperature of 90 to 95 °C. In this Co removal step, all the other above-mentioned elements, except for Cd and Tl, were removed. Normally, therefore, the purification based on As as an activator comprised two steps; first a Co removal step with As_2O_3 addition and a subsequent Cd /Tl removal step with only zinc powder.

The two precipitates produced in the purification, the so-called Co and Cd cakes, were used as raw material for Cu and Cd production - the Cu cake was sold to Cu smelters, whereas metallic Cd was normally produced at the zinc plant.

1.5. The process operated in Kokkola in 1972

The Kokkola plant was started in 1969 with a process compiled from conventional technologies available at that time. A simplified flowsheet is displayed in Fig.3.

The leaching operation comprised initially only a two-step neutral leach, but a license for a two-step Jarosite Process was bought and the process was added in 1971.

In the purification, As was used as "activator" for the Co removal. The temperature in the Co removal was maintained at about 90 °C. The high temperature kept the overpotential for H_2 formation low, which also kept the co-precipitation of Cd at a relatively low level. Eventually precipitated Cd would re-dissolve under H_2 gas evolution. A Zn rich, but else a rather clean Cd precipitate at high recovery was then obtained.

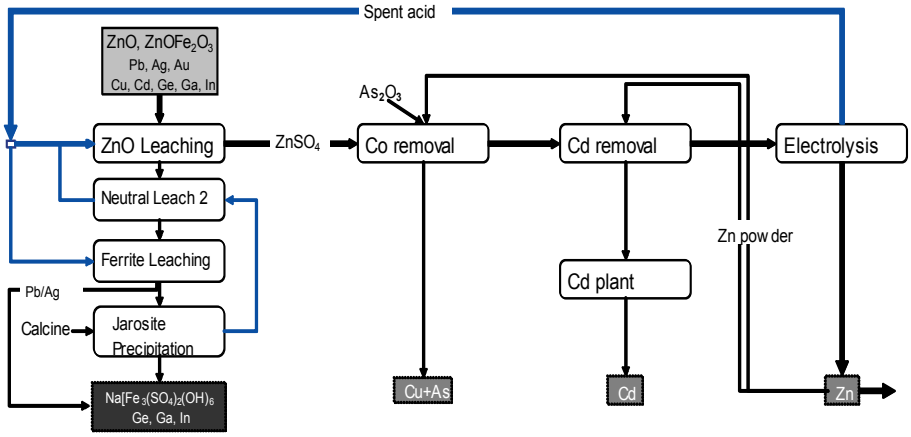

Fig. 3. Flowsheet of the leach and purification operation at the Kokkola plant in 1972.

1. 6. Performance and development state of the process in Kokkola in 1972

1.6.1 Leaching

The jarosite process had been introduced as a two-step process, i.e. ferrite leaching and iron precipitation, as shown in Fig 3. Expectations were that except for increased Zn recovery, the ferrite leaching step should produce a Pb/Ag/Au leach residue, from which these elements could be recovered. In Kokkola, with no adjacent Pb smelter, this implied that a marketable product had to be produced.

It had, however, become clear that, in practice this two-step set-up was insufficient to produce a high grade leach residue, which would allow any economically viable recovery of Pb, Ag and Au from an average concentrate feed composition.

Moreover, as pure ZnO was not available in sufficient quantities for the jarosite precipitation (reaction 8) at any plant, calcine had to be used for neutralization. Since the ferrite in this neutralizing calcine was not leached, the losses of Zn with the jarosite were considerable. The solution from the ferrite leach contained 30 g/l H_2SO_4, which also had to be neutralized in the Fe precipitation step. This added an extra 60 to 70% to the requirement of neutralizing calcine for the jarosite precipitation. Accordingly, the recovery of Zn had only been increased from about 88 to 92% by the introduction of this simple jarosite process.

The development work to overcome these drawbacks, mostly performed by the inventor Georg Steintveit, led to proposals for addition of a number of steps aimed at improving the basic process [14]. A thorough description of development done on the conventional jarosite process was presented 1980 by Arregui *et al.* [15]. In 1972 the developed jarosite process comprised following additional steps:

- to improve the quality of the Pb/Ag, residue the ferrite leaching was operated counter-currently in two, and even three steps [15], enabling to reach 80 to 100 g/l H_2SO_4 concentration in the final step.
- to reduce the need for calcine in the Fe precipitation step, a pre-neutralization step was added to neutralize the excess acid from the leaching [16].
- an “acid wash” step on the jarosite was introduced to recover the contained ferrite zinc. It had been found that at suitable acid concentrations the ferrite could be leached selectively from precipitated jarosite [17].

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By addition of these extra steps, the recovery of Zn was foreseen to be about 98%. From Fig. 4 and 5 where the flowsheets of the “basic” process used in Kokkola and the “developed” processes are shown, the development had led, however, to a complicated and expensive operation. No plant had the developed jarosite process in operation in 1972.

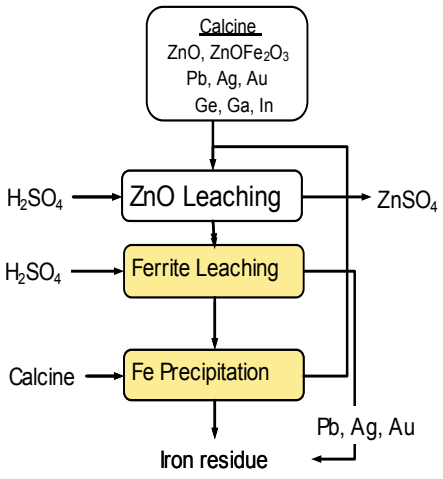


Fig. 4. Leaching in Kokkola in 1972.

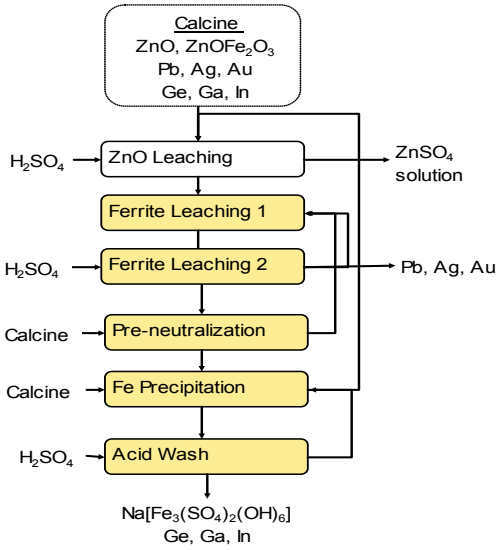


Fig. 5. “Developed” Jarosite process.

1.6.2 Purification

The “hot arsenic zinc dust” purification for Co removal, which was operated in Kokkola, was preformed at 90 to 95 ℃ and the feed solution should contain at least 400 mg/l of Cu. If it was lower, external $CuSO_4$ had to be added. First 50 to 200 mg/l of As_2O_3 was added, followed by shots of Zn powder until a spot test showed a concentration below 0.2 mg/l of Co^{2+}. Average Zn powder consumption was around 5 g/l. The obtained precipitate contained 30 to 50% Cu, 10 to 15% As, about 1% Co + Ni, 1 to 3% Cd and about 10% Zn. As, Sb and Ge were known to precipitate only in this step. This material was fed to the company’s copper smelter where only Cu was recovered, whereas the rest of the metals were largely lost. The ratios of As and Cd to Cu in this material were orders of magnitude higher than in normal Cu concentrates, and therefore, this precipitate represented the major intake of both metals to the smelter. Both elements caused environmental problems, partly by being fumed to the air, and

partly by being routed to costly-to-treat sludge and solutions in the sulfuric acid plant. In addition, in copper smelting, a substantial portion of the As goes to the anode copper, which caused problems in marketing of anode copper. These problems caused the Cu smelter finally to refuse to treat the precipitate.

With the impurity level of the leach solution, the stoichiometric requirement of Zn powder would be around 0.6 to 1 g/l to reduce the impurity elements to the metallic state. Considerable quantities of Zn were, however, consumed through H_2 evolution, and metallic powder had to be left in the purification residue to prevent re-dissolution of the impurities during filtering and hold-ups in the process. All this could bring the powder consumption even up to 5 to 10 times the stoichiometric requirement in zinc plants worldwide. As the zinc in the powder is recycled through the electrolysis, which almost always is the bottle-neck concerning the plant capacity, this Zn reduces the production capacity of marketable metal. If this Zn was sold instead of recycled as powder, it would be charged only with the cost for the concentrate, and thus the profit margin would be the highest possible.

Besides consuming excess Zn dust, the H_2 evolution increased the pH in the purification which caused precipitation of $Zn(OH)_2$ (eq. 11), or more correctly basic Zn sulfates, $(Zn_x(SO_4)_y(OH)_{2(x-y)}$

$$Zn + 2H_2O = Zn(OH)_2 + H_2 \qquad (11)$$

These precipitates passivated the Zn powder surface and made intermediate pH adjustments necessary. This was time consuming, as pH meters were found to be too unreliable and pH at that time was determined through manual titration of acid. Secondly, the basic salts often caused very poor filtering, which occasionally reduced the plants capacity considerably. With the purification operated batchwise, this control was a laborious task and process disturbances occurred frequently.

Metallic Zn in the precipitate, which caused AsH_3 gas evolution if it came in contact with acidic solutions in the working area, was also a source of concern.

In some plants, with a very high Cu content in the solution, Cu removal with only Zn powder was operated as the first step in the purification. Then a part of the Cu was obtained as an As-free product, but with a high Cd content.

In the Cd removal, also a considerable excess of Zn powder was used, and the precipitate contained normally about 60 to 70% Zn and about 20% Cd. In the Cd plant this precipitate was leached with spent acid and Cd was re-precipitated with Zn dust to obtain a precipitate with about 90% Cd. The volume of this leach solution, and thus the size of the equipment in the Cd plant, was thus mostly determined by the Zn content of the “cake”.

1.7. Research and development needs and aims in 1972

The plant had been dimensioned for treating the domestic concentrates, which mounted to about 70 000 t zinc per annum. The actual capacity was, however, found to be about 90 000 t/a, and some concentrate had been purchased from outside. It had become clear, though, that this capacity would be too low to stay competitive in the long run, and an expansion would be necessary.

As most of the technology in the plant had been acquired from outside the company, the research work had to a major part been concerned with gathering knowledge of the existing process and the development being done worldwide. With the expansion project, it became more important to concentrate on the development work and remove as much of the drawbacks of the existing process as possible.

The main flaws of the available leach and purification techniques in industrial operation worldwide could easily be quantified economically from the following data:

- about 7 to 8% of the Zn was lost with the jarosite.
- excess consumption of Zn powder over the stoichiometric need in available purification technologies mounted to an average of about 4 to 7% of Zn production in plants worldwide.
- the obvious lack of knowledge of the chemistry in the purification was substantial and this caused frequently disturbances in the operation and lead to loss of production.
- a Cu product without value was produced in Kokkola.

With the cost structure of a Zn plant, these flaws caused a loss of profit above 5% of the total sales.

Thus the development program for the plant expansion was consequently aimed at

- an economically optimal Jarosite process considering:
  - extractions of Zn, Cu and Cd versus cost,
  - marketable quality of the Pb/Ag/Au residue,
  - maximum utilization of existing equipment.

- a continuous process for the purification with:
    - a solution to the Cu problem
    - reduced Zn powder consumption
    - more stable operation, especially of the Co removal.

2. DEVELOPMENT ON LEACHING [I, II, III, IV]

2.1 New method for leaching of ferrite

To achieve the goals put up for the leaching, a developed Jarosite process was the most obvious choice, as besides available published information also internal studies had shown that Zn recovery of 98%, as well as a reasonable Pb/Ag concentrate should be possible to reach.

The slowest step in the Jarosite process was the leaching of ferrite. This had been studied by Nii, [18], who showed that the leaching rate was proportional to the specific surface area of the ferrite. An in-house study by Saarinen had given the dimensioning data for the leach step in the Kokkola plant [19]. As these studies had been performed at conditions that deferred from the ones prevailing in plant operation, they were not regarded as sufficient base for the plant expansion. The number of different concentrates fed to the plant would also increase and leach kinetics of ferrites for other than the domestic ones were not known.

In experiments (unpublished) made to study possibilities to intensify the ferrite leaching stage, it was unexpectedly noted that jarosite was precipitating in leaching experiments designed to give a Fe^{3+} concentration of up to 80 to 90 g/l at about 40 g/l of H_2SO_4. These experiments were performed at 95 ℃ with spent acid containing NH_4^+ ions on ferrite residue slurries from the plant. The acid concentrations in these experiments were considerably higher than pH 1.5 to 1.3, (about 5 to 8 g/l of H_2SO_4) which, at that time, was generally regarded to be the "jarosite precipitation conditions".

The precipitation rate of jarosite at the high acidities used in these leach experiments was much lower than at the conditions practiced in the jarosite precipitation in the plant, and the precipitation started first after a long incubation time. It was, however, noted that the precipitation rate increased when jarosite had formed and started earlier if the ferrite material contained jarosite. Thus it was obvious that the quality of the Pb residue would at least be very sensitive to any incoming jarosite to the ferrite leach, either through re-circulation with thickener overflows in the process, or precipitated in the preceding neutral leach steps. An option to lower the possibility of iron precipitation would be to lower the HN_4^+ concentration in the circulating plant solution. This would, however, imply working with lower NH_4^+ surplus in the jarosite precipitation stage, and as this stage was straight in the production line, difficulties in the precipitation of iron could cause loss of production. Simple means to completely avoid jarosite precipitation were thus not at hand, and production of a marketable Pb residue became very questionable. This leaching option of ferrite had than to be abandoned.

However, jarosite precipitation during ferrite leaching meant that two reactions had been taking place simultaneously:

$$3ZnOFe_2O_3 + 12H_2SO_4 => 3ZnSO_4 + 3Fe_2(SO_4)_3 \quad (12)$$

$$3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 6H_2O => 2NH_4[Fe_3(SO_4)_2(OH)_6] + 6H_2SO_4 \quad (13)$$

giving the overall reaction (14):

$$3ZnOFe_2O_3 + (NH_4)_2SO_4 + 6H_2SO_4 => 2NH_4[Fe_3(SO_4)_2(OH)_6] + 3ZnSO_4 \quad (14)$$

Reactions (14) and (12) show that leaching of ferrite and precipitation of jarosite simultaneously need only half the amount of acid compared to keeping the reactions separate. This meant smaller flow, which would allow for higher iron content in the final solution if the iron precipitation according to reaction (14) could be brought to an industrially working completion. If so, this would lead to a considerably simplified process compared to the developed Jarosite process, as is illustrated by the flowsheets shown in Fig. 6.

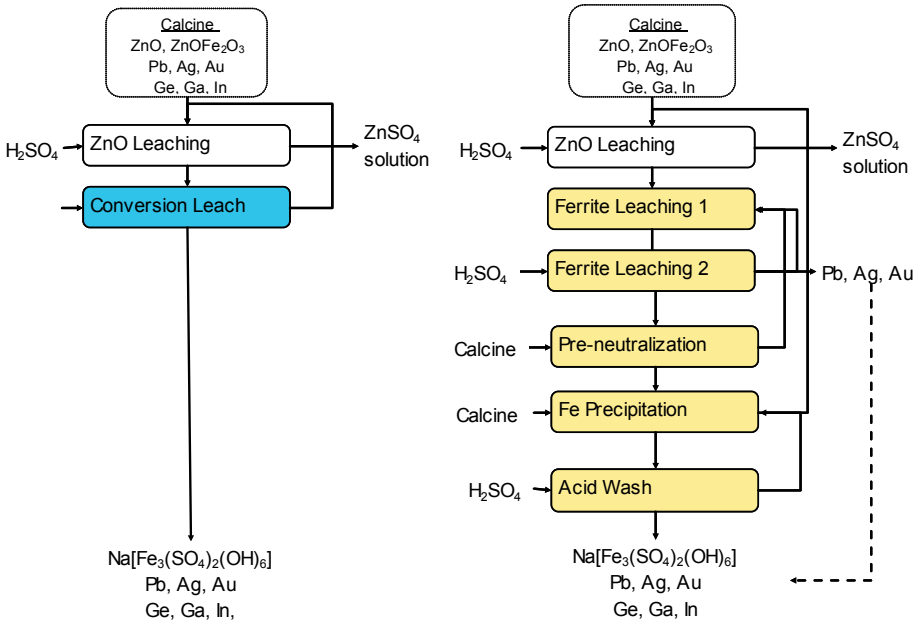


Fig. 6. Comparison of the needed flowsheets to give 98% Zn recovery in the Conversion and the Jarosite process.

Hence, rough process calculations were performed on the obtained preliminary data. The calculations showed very promising possibilities, and a study on the feasibility of using this "conversion" reaction (14) industrially was undertaken.

Unlike the Jarosite Process, with the high acid concentration in this Conversion Process the jarosite precipitation, and not the ferrite leaching, could be the

slowest step. From reaction equation (13) was concluded that the concentrations of Fe^{3+}, NH_4^+ and H^+ should influence on the precipitation rate.

Preliminary conversion experiments at different H_2SO_4 concentrations were performed in laboratory to clarify if the required degree of iron precipitation could be achieved with still an acceptable Zn extraction.

Three leach experiments, two batches and one continuous were performed on ferrite residue from the plant. The residue contained a ferrite concentration equivalent to 46 g/l of Fe, and the amount of spent acid added at the start of the experiments was calculated to give a final H_2SO_4 concentration of 20 respective 30 g/l in the two batch experiments. The continuous run was performed in a 3 reactors co-currently operated set-up.

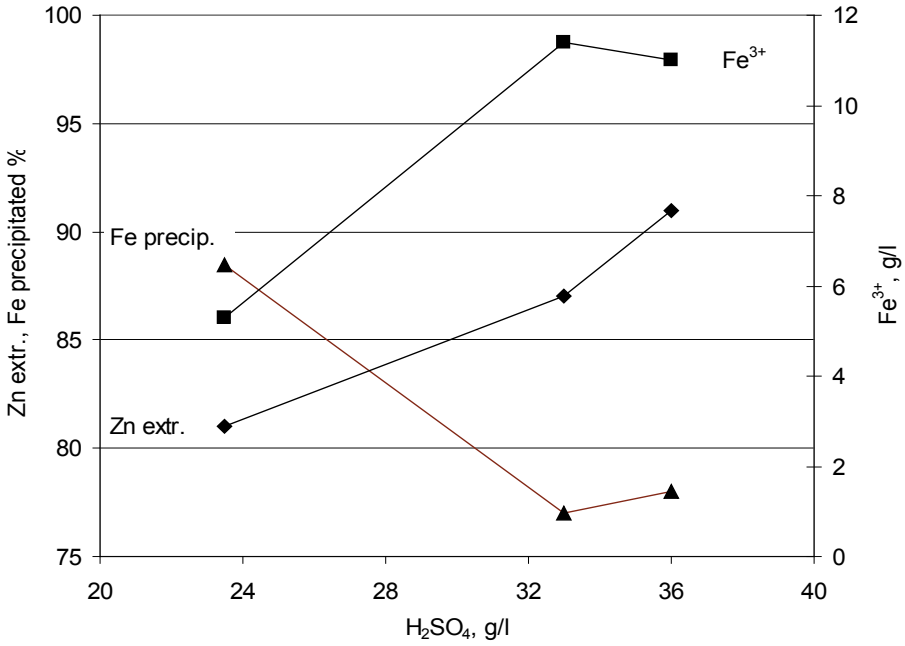


Fig. 7. Conversion leach on ferrite from the plant.
Conditions: 24h reaction time 95 °C, 5g/l NH_4^+, and 100 g/l jarosite seed.
Influence of acid concentration in final solution on Zn extr. = % Zn extraction. Fe precip. = re-precipitated Fe^{3+} in % of leached Fe^{3+} in g/l. Fe^{3+} =

Leaching was performed at 95 °C with spent acid from the plant containing 5g/l of NH_4^+ and 100 g/l of jarosite from the plant was added as seed. After 24 h the residual acid concentrations were 24 respective 33 g/l of H_2SO_4 in the batch experiments and 36 g/l of H_2SO_4 after the third reactor in the continuous one. Results of the experiments are shown graphically in Fig. 7.

The first experiment, which ended at a final acid concentration as low as 23 - 24 g/l, gave a Zn extraction of 81% from the ferrite. This corresponded to about 98% calculated on the Zn in the calcine, which contained about 10% Fe. This extraction was about 3% units higher than what was obtained with the conventional Jarosite Process in the plant.

The final level of iron, 5.4 g/l of Fe^{3+} in solution, obtained in this experiment would be fully acceptable to return to the neutral leach step. With higher final acid concentration, the residual Fe^{3+} concentration in the solution increases sharply.

In the plant, the reactor volume in the whole existing jarosite process allow for only 10 to 12 hours retention time. The rather weak dependence of Zn extraction on final H_2SO_4 concentration made it, however, worthwhile to test the process on plant scale. To operate the process in the plant, only changes in the leaching parameters and minor new piping were required; therefore no extra time for construction of additional equipment was necessary.

The solid-liquid separation after the ferrite leach step was omitted, and the leach slurry was fed directly to the jarosite precipitation reactors were no addition of calcine was made.

The relatively short retention time in the plant, about 12 hours, compared to the 24 h in the experiments, meant that the residual Fe^{3+} concentration in the solution could become critical. This could, however, easily be controlled by starting with a low feed of acid, that would keep the level of iron in solution low during the start-up. The acid addition could then successively be increased until the capacity for ferric iron in the neutral leach was reached.

The final result of this plant experiment showed that without extra investment and operating costs the recovery of Zn in the plant was increased by about 4% over the recovery obtained by the 2-step jarosite process. Of this increase 3% units came from higher extraction from the ferrite and 1% from better filtering properties of the residue which gave a higher washing efficiency.

It was thus evident, that considerable savings in investment would be achieved in the plant expansion project by replacing the developed jarosite process with the Conversion Process. New investment would only be needed for additional reactors and thickeners. These could be provided as large units, which would be considerably less costly than the addition of 4 new steps with a number of small reactors, thickeners, feeding and control systems. In addition, some savings in the operational cost would occur, at least for maintenance.

Furthermore, due to low prices on Pb and Ag and a low fate in a sustainable future for the Pb business at that time (early 1970´s) the loss of Pb/Ag with the jarosite had become a lesser problem. Difficulties to produce a sufficiently

high-grade Pb/Ag residue were also found generally. Even zinc plants with adjacent lead smelter did not treat the residue also if the Zn concentrates contained 5 to 10 times higher levels of Ag than what was foreseen in the future feed to the Kokkola plant. The Pb residues were then deposited, either separately or together with the jarosite like shown in Fig. 6. Consequently, the outlook for production of a marketable Pb residue at the Kokkola plant became very dim.

The Conversion process was accordingly chosen for the plant expansion **[I, III]**.

For the dimensioning of the new leaching circuit and the operation of the process a broader knowledge of the kinetics in the process was needed, and a research program on leaching of ferrite and precipitation of jarosite - both separately and combined, was initiated.

2.2 Jarosite precipitation

2.2.1 Introduction

As seen from Fig.7 preliminary tests on the conversion process had shown that the jarosite precipitation rate was strongly dependent on the acid concentration. According to equation (13) the concentrations of Fe^{3+}, NH_4^+, and SO_4^{2-}, as well as the quantity of jarosite seed, should influence the precipitation rate; - increase with increasing Fe^{3+}, NH_4^+ and SO_4^{2-} and, as seen, decrease with increasing H_2SO_4 concentration.

It could also be assumed that the same components in the solution would influence the solubility of jarosite. This meant that the lowest possible Fe^{3+} level that could be obtained at the end of the leach would increase with the end concentration of acid, - and probably would also NH_4^+ and SO_4^{2-} influence on this level. Accordingly, the solution composition would be important concerning the success of the iron precipitation in a conversion process, and that there would be limitations to how high concentrations of acid could be used.

2.2.2 Jarosite solubility in acid solution

The equilibrium for reaction

$$2NH_4[Fe_3(SO)_4)_2(OH)_6] + 6H_2SO_4 <=> 2NH_4^+ + 6Fe^{3+} + 10SO_4^{2-} + 12H_2O \quad (15)$$

was investigated by leaching a jarosite from the plant in a synthetic solution of 100 g/l Zn^{2+} at 95 ℃. H_2SO_4 was added to the slurry at certain intervals. To allow for sufficient time to reach equilibrium of the reaction, the time between the acid additions was 24 h, where after a sample of the solution was analyzed for Fe and H_2SO_4, and the acid level was then increased. The Fe^{3+} concentration as function of H_2SO_4 concentration obtained in two experiments, with respectively 0 and 5 g/l NH_4^+ added to the start solution, are displayed in Fig. 8a.

In plant solutions the SO_4^{2-} concentration is rather constant, about 350 g/l, and its concentration would be reduced by only about 5 - 7% by the jarosite precipitation, and consequently, when working with plant solutions the SO_4^{2-} concentration was regarded being constant, and its influence was not studied.

Assuming that the solubility of the jarosite at equilibrium follows a power law:

$$\boldsymbol{K_{sp}} = [Fe^{3+}]^{\boldsymbol{nFe}} * [NH_4^+]^{\boldsymbol{nNH}} * [H_2SO_4]^{\boldsymbol{nA}} \quad (16)$$

where K_{sp} is the conditional solubility constant in a plant solution and n_{Fe} etc are the reaction orders with respect to the components. Consequently, the conditional equilibrium concentration of Fe^{3+} in the plant solution will be:

$$[Fe^{3+}] = (\boldsymbol{K_{sp}}/[NH_4^+]^{\boldsymbol{nNH}} * [H_2SO_4]^{\boldsymbol{nA}})^{1/nFe} \quad (17)$$

or

$$[Fe^{3+}] = \boldsymbol{K_{sp}} /[NH_4^+]^{\boldsymbol{nNH}} * [H_2SO_4]^{\boldsymbol{nA}} \quad (18)$$

Optimization with ModEst software gave $\boldsymbol{K_{sp}}$ = 0.00485, nFe = 0.927, nNH = -0.59 and nA = 2.13 The degree of explanation, R^2 = 0.997. The results are shown graphically in Fig. 8a.

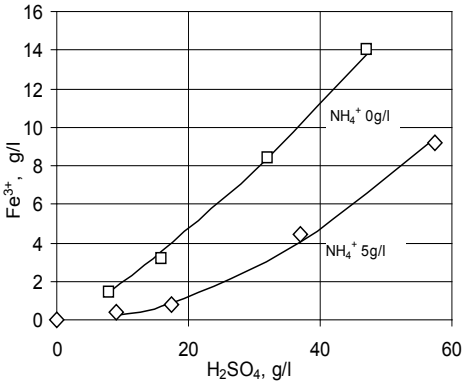


Fig. 8a. Experimentally obtained solubility, given in g/l Fe^{3+}, of a NH_4-jarosite as function of H_2SO_4 and NH_4^+ concentrations.

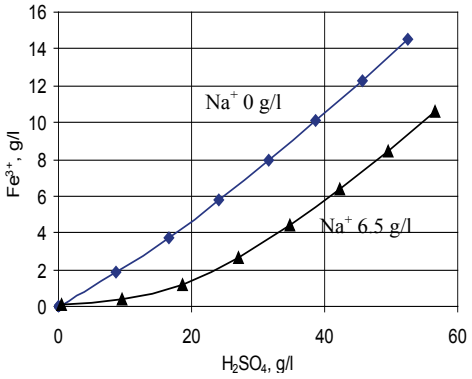


Fig. 8b. Calculated solubility of a Na-jarosite, given in g/l Fe^{3+}, as function of H_2SO_4 and Na^+ concentrations.

To investigate how the experimentally obtained solubilities agree with thermodynamic data, the solubility of Na-jarosite was calculated with Outotec HSC 7, Equilibrium Compositions module [20]. Na-jarosite was chosen, because NH_4-jarosite was not in the database, and the solubilities of these two jarosites are very similar.

In the calculations (Fig. 8b) the same molar concentration of all soluble salts as in the experiments was used. All soluble components (simple and complex ions as well as un-dissociated salts) that according to the HSC database can exist in such a solution were included. Calculations were performed on two different start solutions; one with no Na^+ added and one with 6.5 g/l Na^+, which is about the same molar concentration as 5 g/l of NH_4^+. The results of the calculation are revealed in Fig 8b.

The displayed results in Fig. 8b show a very good agreement with the experimental data in Fig 8a. This implies that it might be possible to obtain reliable thermodynamic models of processes where jarosite precipitation takes part.

In the ferrite leach step of a two-step jarosite process, the final Fe^{3+} concentration will normally be in the order of 25 to 30 g/l, and hence Fig. 8a and 8b illustrate also the difficulties in avoiding jarosite precipitation in this step, even at an acid concentration of 40 g/l and above. This explains why two and even three step counter-current stages was found to be needed in the ferrite leaching to produce a reasonable Pb/Ag residue in the developed jarosite process.

2.2.3. Modeling of jarosite precipitation kinetics 1975

Fig. 7 shows that the extraction of Zn from the ferrite is improved by about 10% units with an increase of the acid concentration from 23 to 33 g/l, whereas the iron content of the solution has more than doubled. Consequently, the kinetics in jarosite precipitation at higher acid concentrations was a major question. In the plant this was learnt by trial and error, but a more scientific approach was decided to carry out.

This was performed by Virtanen in his master thesis, where a series of batch experiments in laboratory were made on hydrolytic precipitation of jarosite from solutions with varying Fe^{3+}, H_2SO_4 and NH_4^+ concentrations [21]. Concentrations in the initial solutions are shown in Table 2. In all experiments 100 g/l of Zn as sulfate and 100 g/l jarosite seed were added. The slurries were heated to 95 °C and kept stirred for 24 h. The final concentrations varied for Fe^{3+}, H_2SO_4 and NH_4^+ between 10 and 20, 50 and 70 and 1 and 12 g/l respectively.

Table 2. Start solutions in Virtanen´s experimental series.

Exp. no	Fe, g/l	H_2SO_4	NH4, g/l
1	44.0	12.3	16.1
2	45.7	19.6	16.0
3	32.7	19.4	10.1
4	33.8	25.0	9.8
5	33.4	17.6	4.9
6	35.4	23.3	5.1
7	35.2	17.2	2.9
8	37.7	23.3	3.2

A summary of these investigations on the kinetics of jarosite precipitation was given in a paper published in 1979 [**IV**]. Here a power law model:

$$-d(Fe^{3+})/dt = k*[Fe^{3+}]^{\alpha}* [H_2SO_4]^{\beta}* [NH_4^+]^{\gamma}* [jar]^{\delta} \qquad [19]$$

for the iron precipitation was applied, and the obtained values for the different reaction orders were: $\alpha \sim 1.9$ to 2, .$\beta \sim -3.5$ to - 2.2, $\gamma \sim 0.5$ to 0.7 and $\delta \sim 0.8$ to 1.4, and as seen, a considerable variation was obtained in the determined values for the individual experiments.

2.2.3.1 Resent modeling of jarosite precipitation on Virtanens data

With all other conditions being constant, the final results of the jarosite precipitation should be determined only by the Fe^{3+}, H_2SO_4 and NH_4^+ concentrations in the start solution. As no reagents are added, the precipitation (reaction 13), is just a crystallization, for which Avrami developed a model [22]. The remaining Fe^{3+} in solution, X, as a function of time is then described as

$$X = 1- e^{-kt\hat{}n} \text{ or } X = 1 - \exp(-kt^n) \qquad (20)$$

According to Kabai who applied this model to leaching of oxides, the parameter *k* is a function of the experimental conditions, whereas *n* is a function of the properties of the solid phase, such as grain size and geometry [23]. This model has now been applied to the results of Virtanen's experiments by assuming a power law influence of Fe^{3+}, H_2SO_4 and NH_4^+ concentrations, (marked [Fe], [A] and [NH] and the corresponding exponents n_{Fe}, n_A and n_{NH} in equation 19) on the precipitation rate. This gives the development of the Fe^{3+} concentration with time as

$$[Fe^{3+}]_t = (1 - e^{(-k1*[Fe]^{\wedge} nFe *[A]^{\wedge}nA*[NH]^{\wedge}nN*t^{\wedge}n)})*[Fe^{3+}{}_0] \qquad (21)$$

The modeling, with all concentrations in g/l, was performed on Excel. The correlation of the model to the obtained experimental data is displayed in Table 3 and Fig. 9, pictures 1 to 8. As seen, good correlation to the experimentally obtained values for the remaining Fe^{3+} was achieved. The model will not go to equilibrium, which the precipitation reactions, due to the solubility of the jarosite in acid solutions, will. Thus the model is valid only within the experimentally examined region.

Table 3. Estimated parameters in the models for jarosite solubility and precipitation.

Jarosite solubility		**Residual Fe^{3+} in solution**	
k_{eq}	0.00485	k	0.0223
n_{Fe}	0.927	n_{Fe}	1.02
n_{NH}	-0.59	n_{NH}	0.352
n_A	2.13	n_A	0.555
		n	-0.464
R^2	0.997	R2	0.976

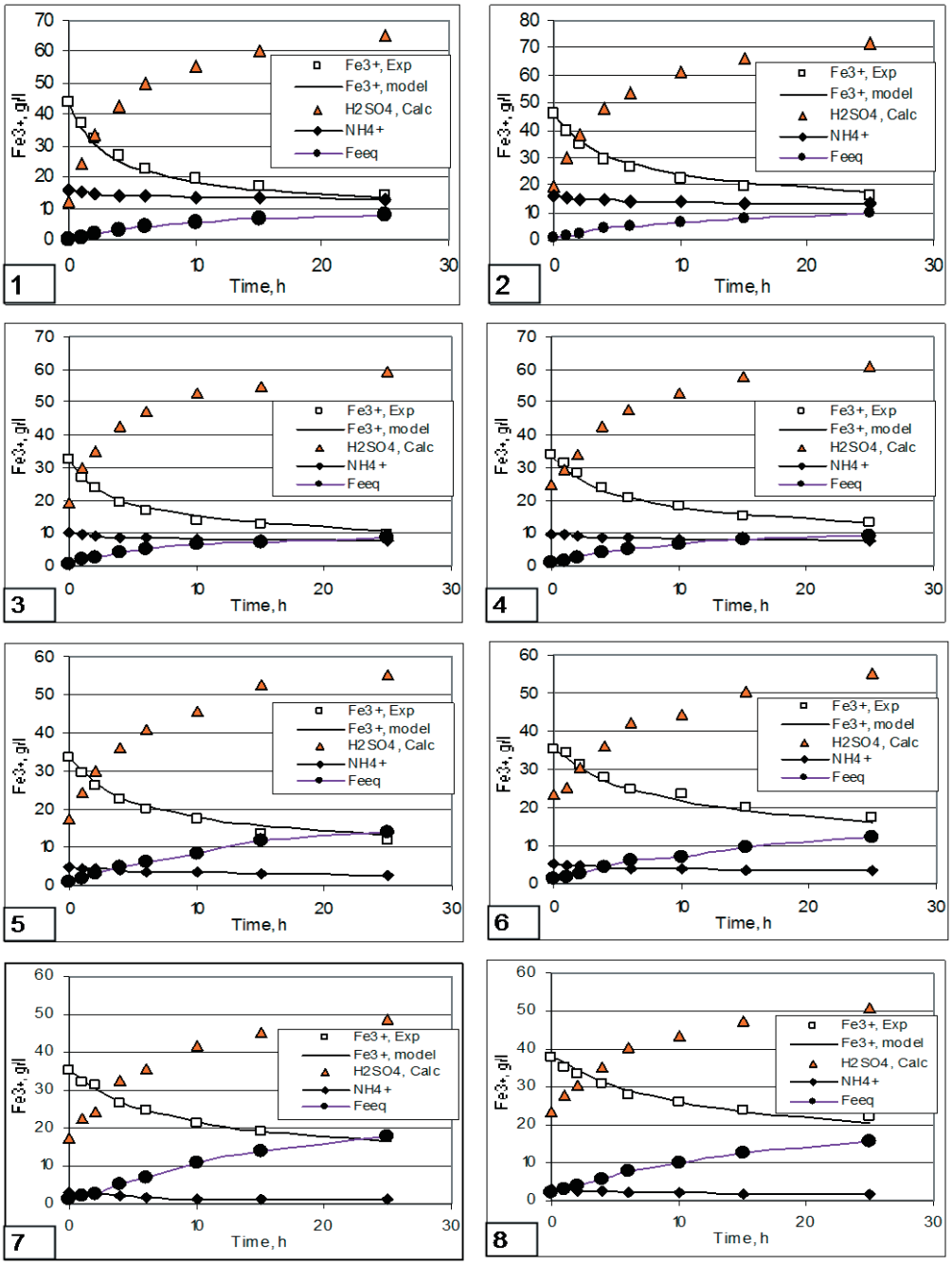


Fig. 9. Hydrolytic precipitation of Fe^{3+} as jarosite from ferric iron solution. Avrami power law model estimation for residual Fe^{3+} (——), as a function of the concentrations at zero time of Fe^{3+}, (9), H_2SO_4, (>), and NH_4^+ given in Table 3. 95 °C and 100 g/l Zn^{2+} jarosite seed in all experiments.

2.2.4. Kinetics of ferrite leaching

Nii *et al*. [25] had studied extensively the influence of conditions during formation of the ferrite on its dissolution rate in acid media. He found that the leaching rate was proportional to the specific surface area of the ferrite, and the leach rate for a single spherical particle was thus described by:

$$dX/dt = kS_0(1 - X)^{2/3} \quad (22)$$

giving the conversion, X, as a function of time:

$$X = 1 - (1- kS_0\, t /3)^3 \quad (23)$$

where S_0 is the specific surface area at zero time. The surface area was determined by nitrogen adsorption. An approximately straight line for $1-(1-X)^{1/3}$, as a function of the leach time, was obtained up to a conversion of about 70 to 80%. At the initial stage of the leach, the obtained rates were, however, somewhat above the calculated, and at the end they were below. Nii concluded that these systematic deviations were due to the broad grain size distribution of the tested material; as a straight line will be obtained only for a material with a single grain size. The activation energy, E_a, was estimated to 67 kJ/mol and it was concluded that the reaction was chemically controlled.

During the planning stage for the conventional jarosite process Saarinen had made the leach experiments both with synthetic ferrite and ferrite obtained from calcine produced in a roasting pilot unit [19]. The concentrate roasted in this pilot was the one being the main feed to the plant in Kokkola. The leach experiments were made at H_2SO_4 concentrations from 10 to 150 g/l and temperatures from 50 to 95 °C and a solid density of only 1.5 g/l of ferrite. The specific surface area of the materials, determined by N_2 gas adsorption, varied from 2 to 13m^2/g. In most experiments, a straight line for $1-(1-X)^{1/3}$ versus leach time was obtained, indicated kinetic control and the leach rate seemed to be clearly dependent on the specific surface area. The test material from the pilot plant roasting campaign had a specific surface area of 13 m^2/g, and was completely leached in 2h at 30 g/l H_2SO_4. This gave a very optimistic picture of the conditions needed to leach the ferrite. The ferrite obtained in the plant had, however, a substantially lower specific surface area and this led to under-dimensioning of the ferrite leach for the initial jarosite process, and new experimental data were needed for the planned expansion of the plant.

To obtain more exact knowledge about the new process which had been adopted in the plant expansion, Virtanen [21] and Björkqvist [24] performed leach series on ferrite from plant calcine in solutions containing 100 g/l of Zn. In the first experiments, with 6 g/l ferrite residue at 95 °C, the leaching time was 2 hours. The $1-(1-X)^{1/3}$ line clearly dropped with time in these experiments, and even before 70% extraction was reached. Thus the rate data

obtained at low extractions could not be extrapolated into the 90 - 95% extraction region, where rough estimates had indicated the economical optimum to be. With the average Fe content of the concentrate fed to the plant, this meant about 99 to 99.5% extraction calculated on the Zn in the calcine. In later experiments the leach time was then chosen to give an extraction at this level. Depending on the acid concentration this required 15 to 50 hours leach time.

SEM and surface area determinations by gas adsorption made by Björkqvist showed that the particles had uneven forms and the specific surface area showed only a minor decrease with increased particle size. At least the bigger particles showed a sponge-like surface and it was concluded that the particles were partially porous. Despite porous structure the leaching of the bigger particles was much slower than for the smaller ones; and thus the leaching, at least of the bigger particles; took place mainly on the outer surface. Björkqvist assumed that the solution inside the particles was quickly neutralized and the leach rate would be dependent on diffusion, and thus the inside leaching was negligible compared to the rate on the external surface.

With the expansion of the plant a number of new concentrates had to be purchased, and the plant should be able to treat an increasing variety of feed stocks, and the influence of the concentrate composition had to be known.

It was found from the leach studies, that the leaching rate for the ferrites varied considerably with different concentrates, and this would influence on the value of a concentrate for the plant. To obtain a sound basis for the evaluation of new concentrates, studies were continued to find a suitable testing procedure. A range of different concentrates were roasted and the ferrite was separated and leached in laboratory scale. In the experimental procedure the ferrites were separated into 10 grain size fractions and the specific surface area for each fraction was determined by N_2 adsorption. The leach rate, at 95 ℃ and 30 g/l H_2SO_4, was determined for each fraction. From these data the leaching characteristics for the different ferrites could be compared, and the expected leach recovery in the set-up of the plant equipment could be estimated for each concentrate. This would facilitate the purchasing of the economically optimal concentrates. The results of this study were presented in 1979 [**IV**].
This procedure for concentrate characterization was, however, rather laborious and did not become extensively used. Characterization was instead simply done by performing standard leaching experiments, under plant conditions, on the un-fractioned ferrite. The evaluation was then done without determination of the rate constants, but by comparing extraction versus time with materials for which plant experience was available.

A mathematical model for the leaching kinetics would, however, be of interest, especially a simple one based on the parameters regularly determined in the process control system. In the leaching of ferrite this was only the concentrations of H_2SO_4 as the temperature could be kept high (95 °C) because the solution would anyhow be heated to high temperatures in the downstream purification.

In sections 2.2.5 and 2.2.6 are described the testing of two models on the results from a series of seven leach experiments at different acid concentrations made by Virtanen. The H_2SO_4 concentration in the experiments were 19, 27, 30, 37, 43, 50 and 75 g/l, and was in each experiment kept as constant as possible by titration with a strong acid solution. The ferrite residue was prepared from a plant calcine. Temperature was 95 °C and the solution contained also 100 g/l of Zn^{2+}.

2.2.5. Grain size distribution model

The conclusions drawn by Björkqvist that the leaching took place mainly on the outer surface of the particle, implies that only this surface should be determining for the leach rate. Assuming further that no product layer is formed [24] and an identical leach rate on all surfaces, the radius of a spherical particle will determine the time to complete dissolution. The conversion of spherical particles with the initial radius, r_0, is then

$$X = 1 - ((r_0 - kt)/r_0)^3 \quad (24)$$

where t is the reaction time and k the linear (corrosion) leaching rate in length units/unit of time. The conversion for the whole material at time t will than be:

$$X = 3((1 - ((r_{0i} - kt)/r_{0i})^3) * m_{0i}) \quad (25)$$

where m_{0i} is the mass of size fraction i at zero time. Making the assumption that the material consists of spheres, only the grain size distribution obtained through sieve analysis is needed to describe the progress of the leaching. The linear leach rate parameter, k, in the different experiments can then be estimated by regression analysis of obtained leach data.

The model was applied to the seven leach experiments made by Virtanen, [21], and the calculations were performed with the ModEst software. The influence of acid concentration on the leach rate was investigated in the range of 20 to 75 g/l of H_2SO_4. The acid concentration was kept constant by intermittent analyzing of solution samples and addition of acid. Major components in, and size distribution of, the ferrite material is given in Table 4.

More precise size distribution of the major fraction - 38 μm, 61%, was not determined, and a reasonable fit of the model could not be obtained. Hence an estimated size distribution into 3 fractions for this part of the material has been used in the calculations. The estimation is based on data for similar materials for which size distribution below the 38 μm fraction had been determined [**IV**].

Table 4. Screen analysis of the ferrite used in the modeling of Virtanen's experiments.

Fraction, μm	***0 - 10***	***10 - 20***	***20 - 38***	38 - 53	53 - 75	75 - 150	150 - 300
Weight,%	***31***	***10***	***20***	9	4	11	*15*
Components	$ZnOFe_2O_3$	ZnO	$ZnSO_4$	ZnS	$PbSO_4$	$CaSO_4$	SiO_2
Weight,%	73.8	9.8	0.3	1.8	3.2	2.5	2.2

The material was prepared from plant calcine by removing the ZnO by leaching at pH 1.7 with H_2SO_4.

The fit of the grain size model to the experimentally obtained leach data for this material is displayed in Fig.10 and Table 5.

2.2.6. Avrami model

The Avrami model has also been tested on the results from the above described experiments on ferrite leaching. As the same ferrite material was used in all experiments where only the acid concentration was varied, *n* should be constant and only *k* should vary with the acid concentration, if the model is applicable. The results are displayed in Fig. 10 and Table 5.

2.2.6.1 Discussion and comparison of the grain size and Avrami models

Both models were first applied to the individual experiments, with the results displayed in Fig.10 and Table 5 columns 1 and 4. Both models gave practically coincidental results for experiments 2, 3, 4, 5 and 7, with very good fit to the experimental results.

With the grain size distribution model the fit for experiments 1 and 6 is much poorer than for the other experiments, whereas with the Avrami model the fit is good for all experiments. However, in experiments 1 and 6 the parameter, *n*, in the Avrami model diverge substantially from the rather constant values obtained for experiments 2, 3, 4, 5 and 7.

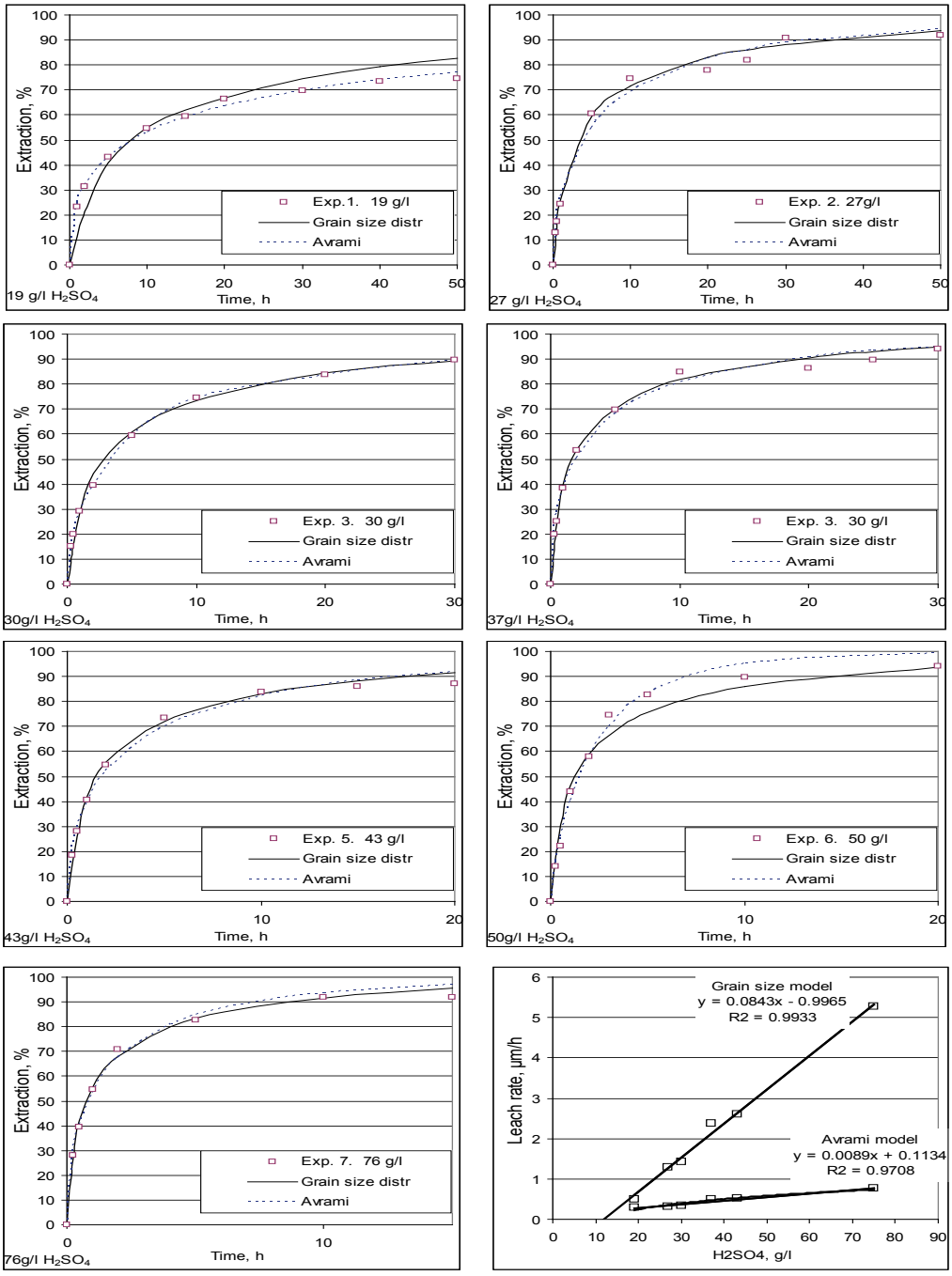


Fig. 10. Fit of the Grain-size population and Avrami models to the individual ferrite leach experiments at 19 to 76 g/l H_2SO_4 and 95 °C. The bottom right diagram show the obtained values for the rate constants as a function of H_2SO_4 concentration with calculated trend lines.

Examination made on the experimental data, revealed that during the first hours, the extraction in experiment 6 is much too low to fit into the trend for the rest of the experiments. The reason for this deviation could not be identified, but some mistake had obviously occurred in the experimental procedure.

In the experiment with 19 g/l H_2SO_4, the experimental data seem to bend off faster than the prediction of the grain size model. Any explanation for this deviation was not found from the published experimental data. Possible explanations could be lower than reported temperature or acid concentration towards the end of the experiment, or an occurring passivation; meaning that the solubility limit for the ferrite is being reached at this, the lowest, acid concentration applied in the series. No own studies, which could clarify if this could be the cause were done, and neither has any experimental data from studies on the solubility of industrially produced Zn ferrite in zinc plant solutions been found in the literature.

The constant value for n, obtained with the Avrami model in experiments 2, 3,4,5,7, indicates that the model could be applicable for describing the kinetics in acid leaching of ferrite.

Trend lines for the leaching rate as a function of the acid concentration in the grain-size and the Avrami models are displayed in the bottom right diagram in Fig 10. These obtained rate expressions and the mean values for n from experiments 2-5 and 7 were used in a new calculation, and the results are displayed in Fig. 11 and in columns 2 and 5 in Table 5.

The two models coincide now fully for experiments 2 to 7, whereas for Exp. 1 both models give substantially higher extractions than experimentally obtained.

Assuming that the poor description of the two models for experiment 1 was caused by approaching the solubility limit for the ferrite, the driving force of the leaching would be influenced by the difference between the equilibrium concentration for Fe^{3+}, C_{Feeqv}, and the actual iron concentration, C_{Fe}, in the solution at the acid concentration in question,. The leach rate constant, k, could then be described both by the acid, C_A, and the Fe^{3+} concentrations:

$$k = k_0 * f(C_A) * f(C_{Feeqv} - C_{Fe}) \tag{26}$$

where k_0 is the rate in absence of Fe^{3+}. If it is further assumed, that the influence of the acid is described by a second order equation, as obtained in the above calculations, (se Fig. 11 bottom right diagram), and, that the influence of ferric iron follows a power function of the difference between the two iron concentrations, k would be:

$$k = k_{0A} * (aC_A^2 + bC_A)^c * (C_{Feeqv} - C_{Fe})^d \quad (27)$$

This expression for *k* has been used in the grain-size model,

$$X = 3((1 - ((r_{0i} - kt)/r_{0i})^3) * m_{0i}) \quad (28)$$

and the parameters in the expression for *k* and the values for C_{Feeqv} as function of the C_A were determined:

$$k_{Lin} = 0.0112*(C_A)^{0.224}*(C_{Feeqv} - C_{Fe})^{0.647} \quad (29)$$

The obtained C_{Feeqv} values, (Table 5 col. 6), were also used in the Avrami model and the obtained expression for the extraction became

$$X = (1-\exp(-0.06C_A{}^{0.30}(C_{Feeqv} - C_{Fe})^{0.282t\wedge(0.55)}) \quad (30)$$

The results of these calculations are displayed in Table 5 and Fig.12, show that the two models give equivalent results for all experiments except for Exp. 6 where neither model give a fit compatible to what is obtained in the other experiments.

Table 5. Variations in the parameters in the Grain-size population and Avrami models applied to a series of ferrite leach experiments at 19 to 76 g/l H_2SO_4 and 95 °C.

		Grain-size population model					
		Column 1		Column 2		Column 3	
Experiments		Individual exp.		k=f([H_2SO_4]		k= f([H_2SO_4], [Fe^{3+}])	
No	H_2SO_4 g/l	kL, $\mu m/h$	R^2	kL $\mu m/h$	R^2	C_{Fqeq}, g/l	R^2
1	19	0.5	**0.865**	0.96	**0.52**	7.7	0.976
2	27	1.3	0.988	1.45	0.986	15.4	0.988
3	30	1.43	0.986	1.64	0.98	16.1	0.985
4	37	2.38	0.988	2.12	0.983	27.7	0.99
5	43	2.61	0.991	2.55	0.991	29.6	0.993
6	50	3.21	**0.971**	3.09	**0.97**	**40**	**0.946**
7	76	5.28	0.994	5.32	0.994	65.3	0.994
Average for			0.99		0.909		0.988
experiments. no			2,3,4,5,7		2,3,4,5,7		1,2,3,4,5,7

		Avrami model							
		Column 4			Column 5		Column 6		
Experiments		Individual exp.			n = 0.55		k= f([H_2SO_4], [Fe^{3+}])		
No	H_2SO_4 g/l	kA	n	R^2	k	R^2	C_{Feeq} g/l	n	R^2
1	19	0.288	**0.418**	0.992	0.2	**0.931**	7.7	0.6	0.993
2	27	0.324	0.561	0.985	0.33	0.985	15.4	0.6	0.980
3	30	0.348	0.568	0.998	0.36	0.997	16.1	0.6	0.993
4	37	0.489	0.530	0.989	0.48	0.988	27.7	0.6	0.988
5	43	0.511	0.532	0.989	0.5	0.988	29.6	0.6	0.988
6	50	**0.517**	**0.769**	0.986	0.57	**0.985**	40	0.6	**0.949**
7	76	0.764	0.558	0.988	0.77	0.993	65.3	0.6	0.991
Average for				0.991		0.98			0.989
experiments. no				1,2,3,4,5,6,7		2,3,4,5,6,7			1,2,3,4,5,7

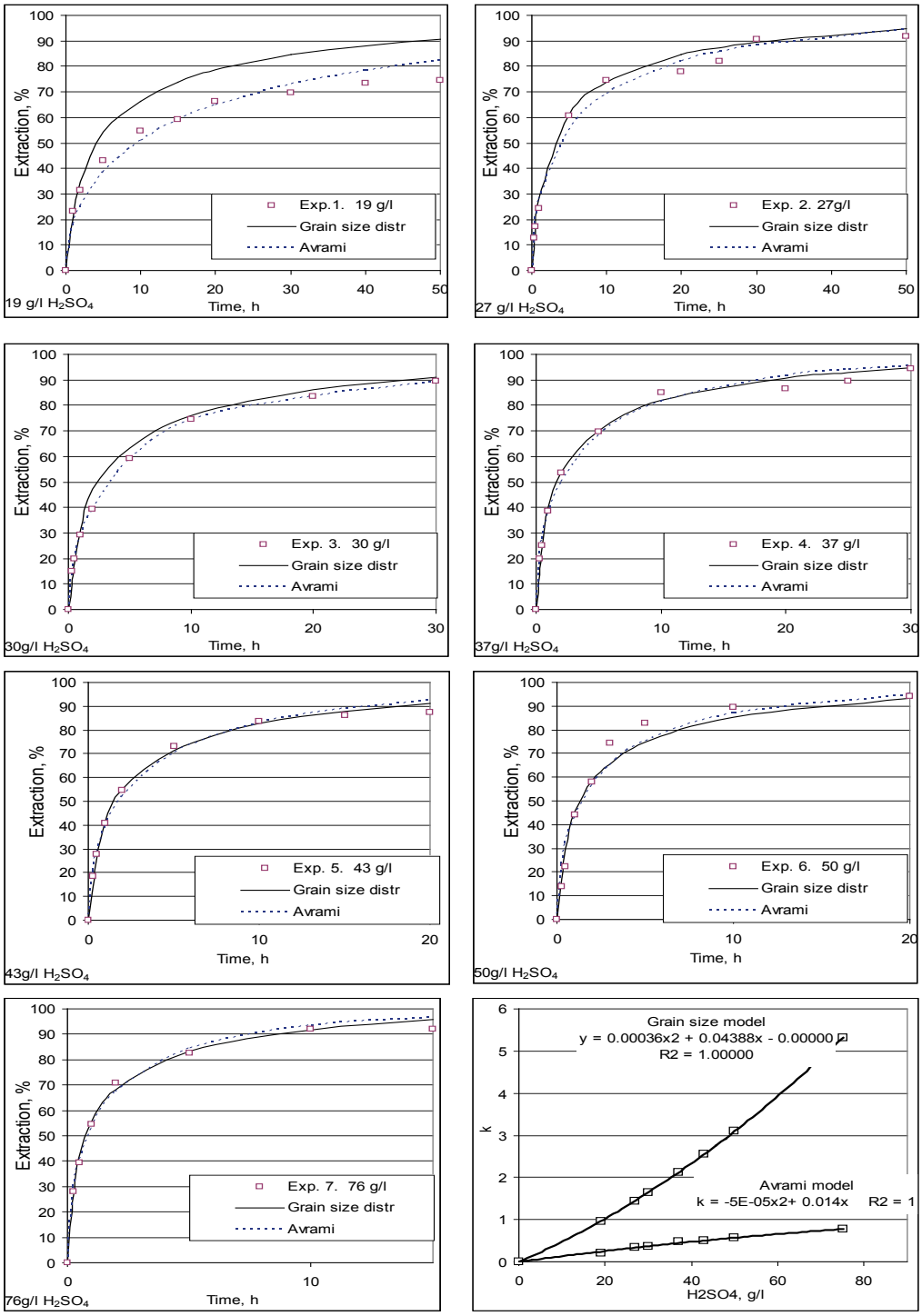


Fig. 11. Fit of the Grain-size population and Avrami models with kL calculated with the f([H_2SO_4]) shown in Fig.10 bottom right diagram, and n in the Avrami models for the mean of Exp.2 -5+7 in the individually optimized.

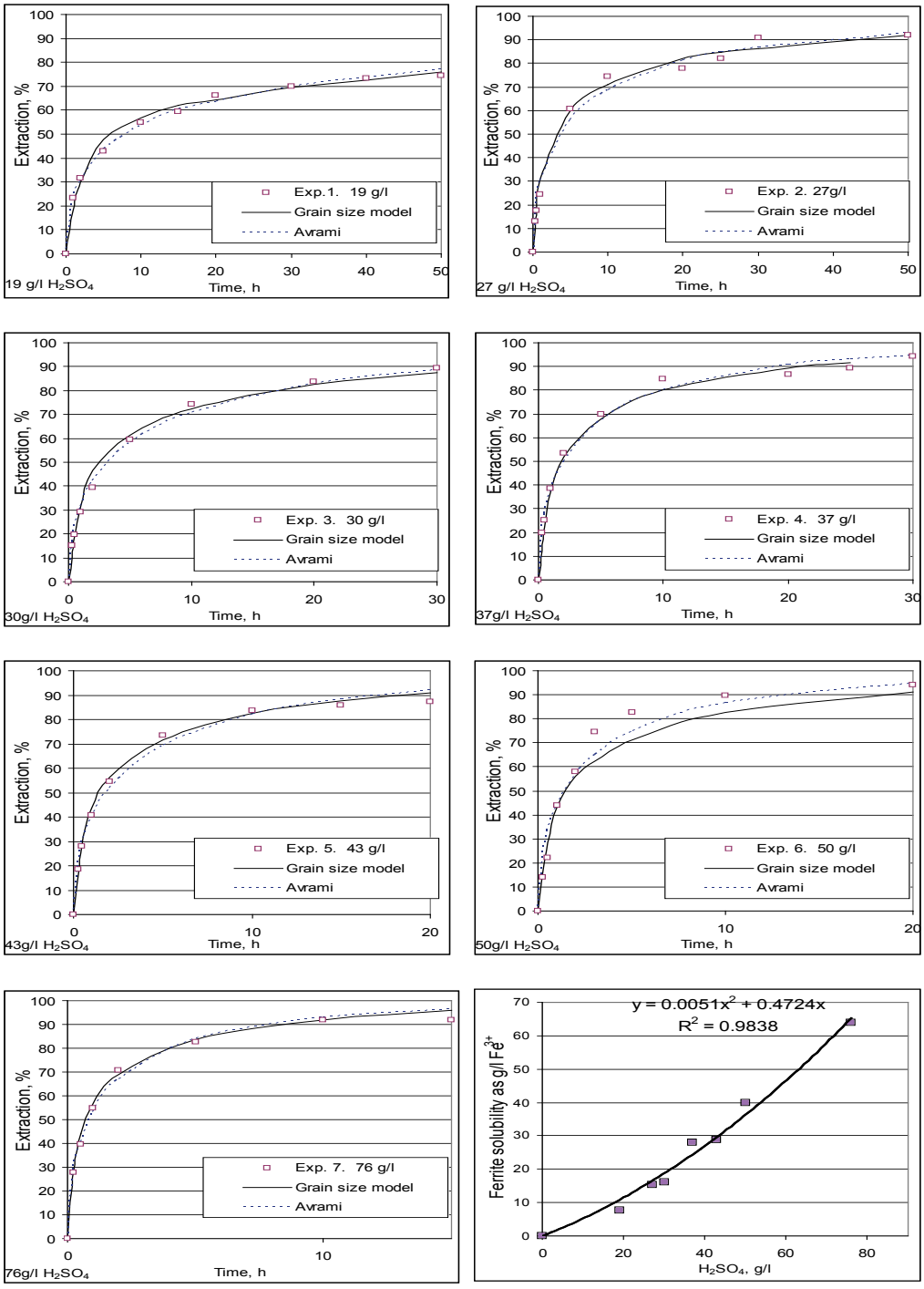


Fig. 12. Fit of the Grain-size population and Avrami models with ***kL*** calculated with the f([H_2SO_4]) shown in Fig.11, last diagram, and ***n*** in the Avrami models is the mean of Exp. 2, .3, 4, 5, 7 in the individual optimization.

No studies on the solubility of industrially produced zinc ferrite in acid, and its eventual influence on zinc extraction have been found in the literature.

The solubility of zinc ferrite as a function of the H_2SO_4 concentration at 95°C was calculated with HSC 6.1 Equilibrium Calculation module. The ferrite used in the calculations is the stoichiometric $ZnFe_2O_4$ in the data base, and all soluble Fe^{3+} and Zn^{2+} complexes with OH^- and SO_4^{2-} given in the database were included in the solution composition.

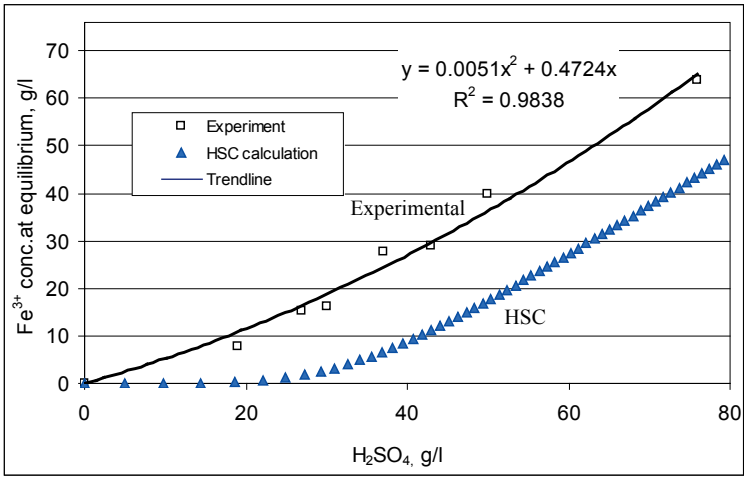


Fig. 13. Comparison of the experimentally obtained solubility of $ZnFe_2O_4$, from Fig.12 last diagram, with the thermodynamic calculations with the HSC program. The solubility is given in g/l of Fe^{3+}.

The Fe^{3+} concentration for the HSC-curve displayed in the diagram is the sum of all soluble Fe-species, and the H_2SO_4 concentration, in g/l, is calculated as the sum of H^+ and HSO_4^- ions minus all OH-complexes. In Fig. 13, the values for Fe_{eq} obtained with the HSC program are compared with the values obtained in the modeling of the above experimental series (Table 5 column 3). Fig.13 shows that the plant ferrite is less stable than the ferrite used for the determination of the data in the HSC database, and especially at low acidities, where the ratio between the experimentally obtained values and the calculated ones is very high.

The formation of the ferrite in the fluid bed roaster could support such a behavior of the plant ferrite. Coarse particles will remain hours at high temperature in the furnace bed, whereas fine ones are blown out of the bed and cooled down only in minutes. The retention time at high temperature will thus be very different for the different size fractions, and likely this will influence the crystal structure and stability of the different ferrite particles. Nii *et al*. [25] found a very strong influence of different conditions during the formation of ferrite, i.e. temperature, atmosphere, cooling rate, on the dissolution rate. The

leaching was, however, performed in a 9% solution, which, according to the observations made in this thesis, implies that any solubility limit would hardly have been noticed.

The solubility of the plant ferrite is much higher than for the computed "HSC ferrite" an assumption that a decrease of the leach rate in Experiment 1 can be caused by approaching the solubility limit of the ferrite cannot be abandoned on the basis of these thermodynamic calculations.

Accordingly, when determining the leach rate of ferrite to be use in process design, also the solubility of the ferrite should be considered; especially, as it seems that normal concentrations of ferrite in plant operations can result in Fe^{3+} concentrations, which can exceed the ferrite solubility limit. Thus experiments performed at lower solid densities can give misleading results regarding the leach rates and time needed to reach extraction targets from ferrite. Accordingly, leach data for process design should not only be determined as a function of acid concentration, but also of the solid concentration.

2.2.7 Studies on the conversion process

To gain more exact knowledge about the process Björkqvist studied the influence of H_2SO_4, ammonium and jarosite seed concentrations on conversion leaching, reaction (14) on page 18, for two different ferrites from the plant [24]. The batch experiments, with 24 hours reaction time, were made with synthetic electrolyte containing 12 g/l of NH_4^+ at 95 °C. One of the ferrites samples was taken from the feed to the conversion process in the plant and contained about 27% jarosite. The other sample was prepared by leaching the ZnO from a sample of plant calcine in a synthetic H_2SO_4 solution to obtain a jarosite free material.

The composition of the starting slurries were calculated to reach concentrations between 25 and 40 g/l of H_2SO_4 and Fe^{3+} concentrations of 5 to 10 g/l at 100% ferrite extraction at the end of the experiment. In the experiments with the plant ferrite (containing jarosite), an amount of ferrite containing 33 g/l iron was added, and with the jarosite-free ferrite residue, the quantity corresponded to 49 g/l of Fe. All reagents were added in the beginning of the experiments. Samples of the solutions were withdrawn at 0.5, 1, 2, 4, 6, 12 and 24 h and analyzed for Fe^{3+} and H_2SO_4. Solids were analyzed at 4, 10, and 25 h for Zn and Fe and the extraction of Zn and the degree of Fe precipitated as jarosite were calculated. It was assumed that the extraction of Fe from the ferrite was equal to the extraction of Zn. Then the Fe precipitated as jarosite = extracted Fe from the ferrite minus Fe^{3+} ions in solution.

A typical example of the progress of the experiments, where ferrite leaching, reaction (12) and jarosite precipitation, reaction (13) take place, is given in Fig. 14.

$$3ZnOFe_2O_3 + 12H_2SO_4 => 3ZnSO_4 + 3Fe_2SO_4 + 12H_2O \quad (12)$$

$$3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 6H_2O => 2NH_4[Fe_3(SO_4)_2(OH)_6] + 6H_2SO_4 \quad (13)$$

The ferrite is leached, reaction (12), very quickly at the high H_2SO_4 concentration at the start of the experiment, and the iron content in the solution increases rapidly. The acid concentration drops to a rather constant level at about 30 g/l H_2SO_4. At this acid concentration, (after about 2h reaction time), the rate of the iron precipitation, reaction (13), exceeds the leaching rate of the ferrite, and iron content in the solution decreases. For the rest of the experiment

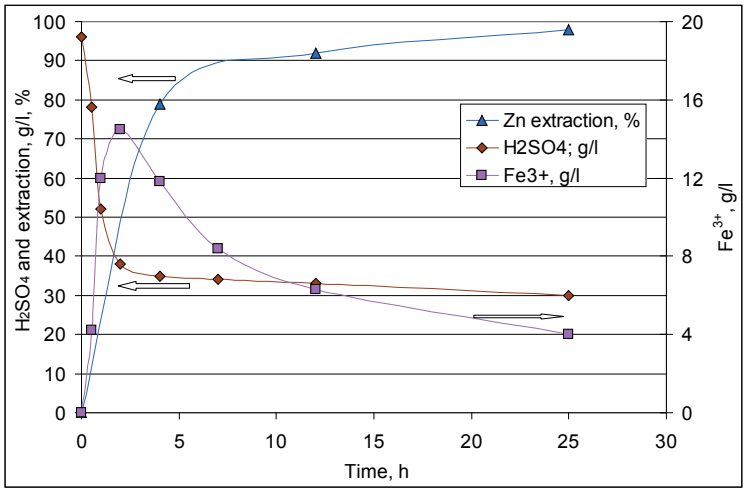


Fig 14. Typical progress of a Conversion experiment at 95 °C.

a balance between the acid liberated in the jarosite formation and the acidconsumed in leaching of the ferrite is reached, and the acid concentration stays fairly constant. The curve marked “Zn extraction” is the same as the extraction of ferrite. In 24 h, the iron in solution was in this experiment reduced to 4 g/l, a level well below the requirement to ensure a safe operation of the neutral leach. The extraction of Zn from the ferrite has also reached about 90%, which also is a very satisfactory result, as 90% extraction from the ferrite means about 99% extraction calculated on the Zn in a calcine containing 10% Fe.

2.2.7.1. Modeling of the conversion process.

A power law model of the conversion process has been applied to the results of nine. 9, conversion experiments made by Björkqvist [24]. Since no particle size distribution was determined on the solid materials only the Avrami model was applied both for the ferrite leaching and the jarosite precipitation.

Ferrite concentration, is given in g/l of ferrite iron, C_F. H_2SO_4, NH_4^+ and jarosite seed concentrations, C_A, C_N and C_J, given in g/l/(g/l of ferrite iron) were varied in the initial slurry. NH_4^+ concentration, C_N, was added as a variable even though it was kept constant at 12 g/l in all experiments, but the C_N to C_F ratio varied slightly in the experiments.

The input data for the model are given in Table 6. The model, reactions (31), (32) and (33), is given as a Fe balance between iron leached from the ferrite, $+\Delta Fe_f$, and iron precipitated as jarosite, $-\Delta Fe_j$. The Zn extraction is equal to the iron extraction from the ferrite. An sub index "$_f$" or "$_j$" is added to the parameters to distinguish between ferrite leaching and jarosite precipitation.

$$+3\Delta Fe_f = (1- \exp(-k_f *(C_A)^{nAf}*(C_F)^{nFf}*t^{n_f}))*C_F \quad (31)$$

$$-3\Delta Fe_j = (1- \exp(-k_j *(C_A)^{nAj}*(C_F)^{nFj}*(C_N)^{nNj}*(C_J)^{nJ}*t^{n_j}))*C_F \quad (32)$$

$$Fe^{3+}{}_{solution} = 3\Delta Fe_f - \Delta Fe_j \quad (33)$$

Table 6. Composition of the starting slurries, final conversions (at 25 h) of Zn and Fe in %, and Fe^{3+} in final solution in the experimental series on the Conversion process.

Exp	Fe_F	H_2SO_4,	NH^+_4,	Jar	Conversion at 25h		Fe^{3+} in final solution	
	C_F	C_A	C_N	C_J			% of C_F and g/l	
no	g/l	g/g Fe_{fer}			Zn,%	Fe,%	%	g/i
1	48.6	2.7	0.25	0.51	90	77	13	5.7
2	48.5	2.72	0.25	1.03	93	74	19	8.6
3	49.6	3.02	0.24	2.02	99	83	16	7.9
4	49.3	2.74	0.24	2.03	98	82	16	7.7
5	49.4	2.65	0.24	2.03	97	86	11	5.3
6	33.2	2.59	0.36	1.20	86	74	12	3.4
7	33.9	2.83	0.35	1.18	96	69	27	8.8
8	33.1	2.90	0.36	2.72	95	80	15	4.7
9	33.1	2.90	0.36	4.23	98	86	12	3.9

The modeling was done both on the two ferrite materials combined, Fig 15a, and separate, fig. 15b. The obtained values for the parameters are given in Table 7.

The fit of the model is slightly better for the two ferrite materials separately, but any trend between the two cannot be seen. This is also to be expected as both ferrite materials might well originate from calcines of a similar blend of concentrates. The concentration of jarosite seed was added as a parameter also in the model of ferrite leaching. This was done because incidents in Kokkola and also two other plants showed in the early days of operation of the Conversion process that leaching of ferrite could cease at an acid concentration as high as 35 – 40 g/l of H_2SO_4. This happened as jarosite precipitation stopped when the recycling of jarosite seed in the circuits were incidentally interrupted. Table 7 does, however, not show that jarosite seed, n_{jar}, should have any clear influence on the leach rate of ferrite, and the incidents in the plants cannot be explained by the results from these experiments.

The cause for the stop in ferrite leaching points strongly to the solubility limit of the ferrite being reached like suggested in section 2.2.6.1.

These difficulties in the plants were overcome by securing sufficient recycling of jarosite, but the ulterior cause was, to my knowledge, never clarified. A separate patent, **(II)**, on the importance of jarosite seed for the precipitation rate of iron in the Conversion process, was published, as this was not sufficiently emphasized in the parent patent.

Table 7. Parameters obtained with the Conversion process model.

Optimized	Reaction	n_{Fe}	n_A	n_{jar}	n_N	k	n	R2
Ferrite 2	Ferr.leach		2.15	0.13		0.088	0.379	0.984
	Jar.precip	0.971	-2.48	0.34	0.09	1.054	0.993	0.935
Ferrite 1	Ferr.leach		3.06	-0.02		0.039	0.337	0.986
	Jar.precip	0.982	-2.26	0.53	-0.06	1.188	0.713	0.986
Ferrite 1+2	Ferr.leach		2.52	0.06		0.062	0.361	0.986
	Jar.precip	0.967	-2.07	0.43	0.07	0.875	0.886	0.975

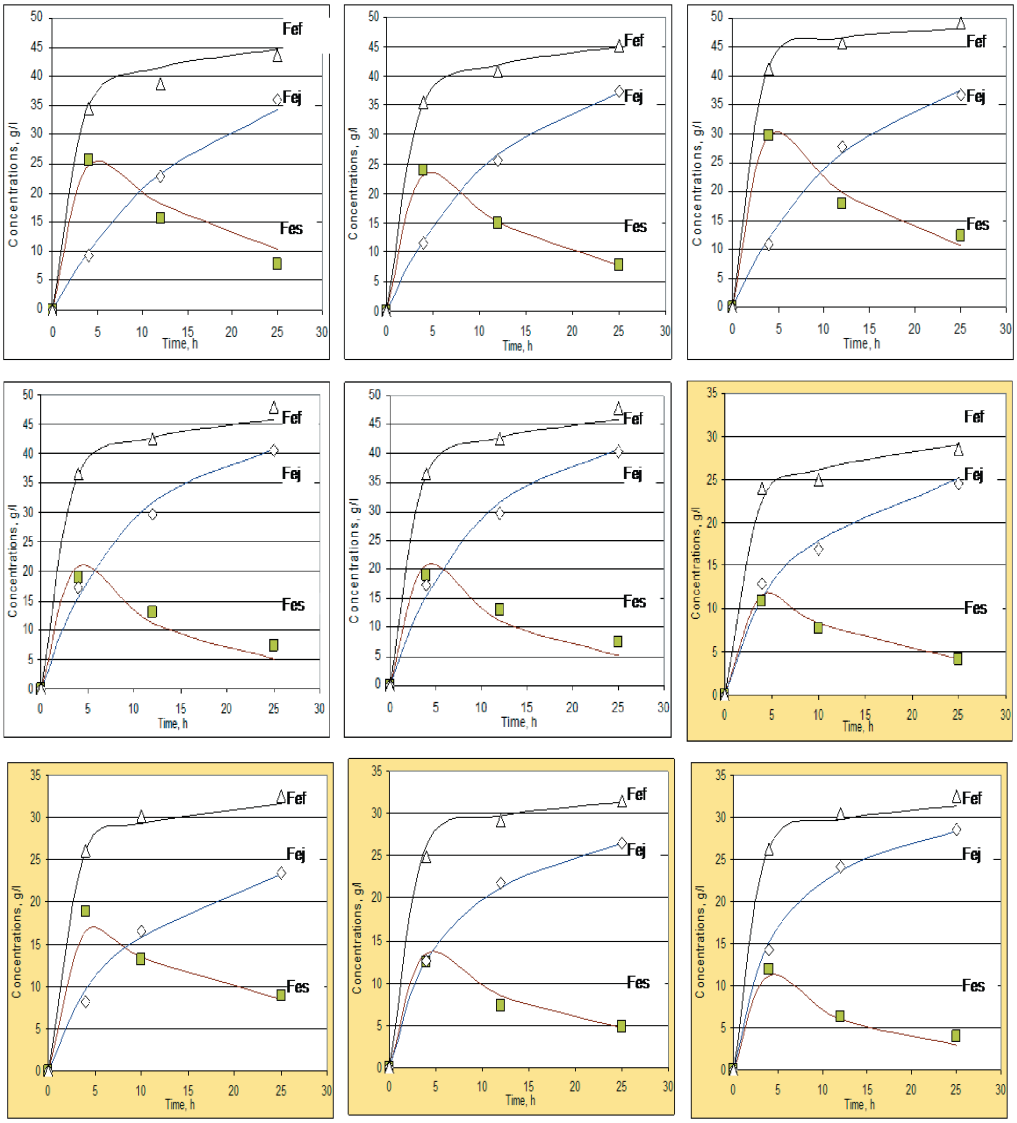


Fig. 15a. Fit of the Avrami model to the behaviour of iron in the Conversion experiments. Separate optimizing of the two ferrite materials: 1 (5 first diagrams) and 2 (last 4 ones). Fef= Ferrite iron leached, Fej = iron precipitated as jarosite, Fes = Fe^{3+} in final solution. All in g/l.

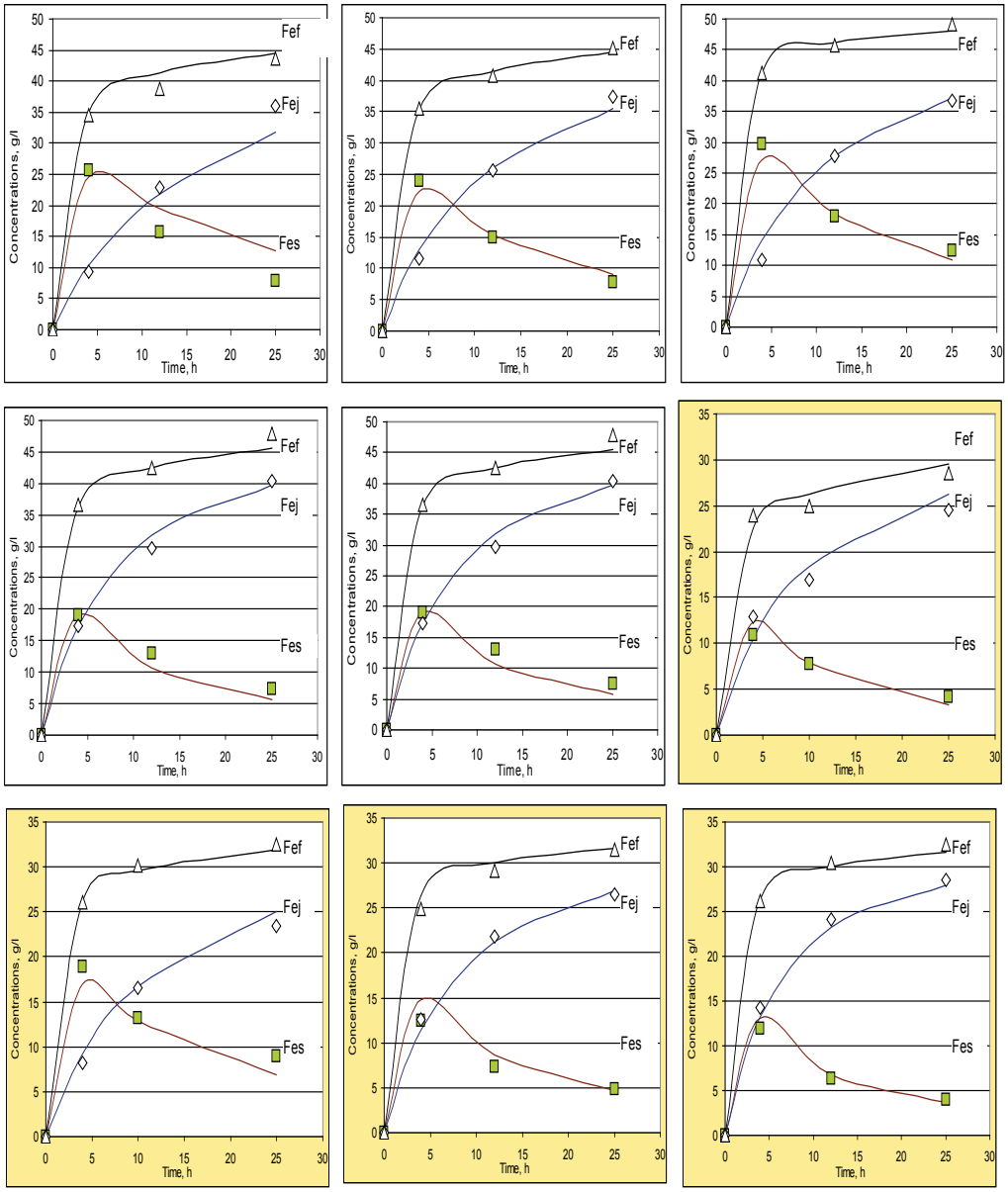


Fig. 15b. Fit of the Avrami model to the behaviour of iron in the Conversion experiments. Combined optimizing of the two ferrite materials: 1 (5 first diagrams) and 2 (last 4 ones). Fef= Ferrite iron leached, Fej = iron precipitated as jarosite, Fes = Fe^{3+} in final solution. All in g/l.

3. DEVELOPMENT ON PURIFICATION [V, VI, VII, VIII, IX]

3.1. Introduction

The main impurities in the leach solution, Cu, Cd, Co, Ni, Pb, Tl, As, Sb and Ge, have to be removed before the electrolysis. These elements are all more electropositive than Zn, and will be reduced together with zinc at the cathode during the electrolysis. Cd, Pb and Tl will simply be deposited with the Zn and contaminate the product, whereas the others will not be found in the metallic zinc to any greater extent.

This co-precipitation of impurities will strongly activate the formation of H_2 gas on the zinc cathode surface. Especially detrimental are the hydride gases forming elements, As, Sb and Ge; and concentrations of only 0.1 mg/l of Sb can totally inhibit the precipitation of zinc.

With all these impurities being nobler than Zn the main technology used for removal is cementation with metallic Zn powder to obtain a metallic precipitate:

$$Me^{n+} + (n/2)Zn = Me + (n/2)Zn^{2+} \quad (34)$$

This reaction is, however, straightforward only for elements such as Cu, which is thermodynamically stable in non-oxidizing aqueous solutions at a pH of 4 to 5. It works also satisfactory with elements like Cd, which similar to Zn is thermodynamically unstable at the prevailing conditions, but is also protected by a high overpotential hydrogen.

Co and Ni which are slightly more electropositive than Cd cannot be precipitated to a sufficient degree in metallic form, - and especially this is pronounced for Co. To improve the precipitation, a number of additives in combination with Zn powder had been tested extensively during the development of the electrolytic process [26]. The process according the patent granted to Electrolytic Zinc Company of Australasia [12] on the method for Co removal, where sodium arsenite was used in the presence of Cu^{2+} and Zn dust was widely used for Co removal in 1970s. At that time, the knowledge of the mechanisms of this purification system was very poor, and the operational practice, which was based more on subjective plant experience than on well understood chemistry, varied from plant to plant. The function of As was not known, and neither had any compounds it formed with Co or other impurities been identified, - and As was referred to as an “activator”. It was also generally regarded that a high concentration (400 - 500 mg/l) of Cu^{2+} in the starting solution, as well as a temperature of 90 °C or higher were needed. If the

solution naturally had a lower Cu^{2+} content, external $CuSO_4$ was added. In this Co removal step all of the above-mentioned elements, except for Cd and Tl, were removed.

A normal purification stage based on arsenic activated Co removal consisted normally of two steps; - the first for Co with As_2O_3 addition and a succeeding Cd removal with Zn powder alone. This purification system was referred to as the "hot arsenic-zinc dust" system.

In some plants, with very high Cu contents in the solution, a separate Cu removal step was added as a first step in the purification. Thus a part of the Cu was obtained as an As-free product. Tl was precipitated together with Cd. The obtained precipitates, so-called Cu respectively Cd "cakes," were used as a raw material for metallic Cu respective Cd production. The Cu cake was normally sold to Cu smelters, whereas metallic Cd was typically produced at the zinc plants.

3.1.1 Co purification practice in early 1970s.

The "hot arsenic-zinc dust" purification for Co removal was preformed at 85 to 95 ℃ with the solution containing at least 400 mg/l Cu. 50 to 200 mg/l As_2O_3 was added, followed by Zn powder additions until a color spot test for Co showed a content of less than 0.2 mg/l. Depending on the Co content of the feed solution, the Zn powder consumption varied widely, from 5 g/l and upwards [27]. The Co precipitate contained 30 to 50% of Cu, 3 to 15% of As. Co and Ni, dependent on their concentration in the feed solution, - occurred in concentrations around 1%. Cd and Zn contents were from 1 to 3 and about 10%, respectively. This cake was then normally fed to copper smelters, where only Cu was recovered. The rest of the metals were largely lost.

Because the ratios of both As and Cd to Cu in the Co-cake were orders of magnitude higher than in normal Cu concentrates, the "Cu-cake" could stand for a substantial quantity of the intake of these two elements to a smelter. They both caused environmental problems in the Cu smelter, partly by being fumed to the gas phase and partly by going to costly-to-treat sludge and solutions in the sulfuric acid plant. In addition, a considerable portion of the As ended up in the copper anode and caused problems in marketing of this product.

For a normal impure solution, the stoichiometric requirement for Zn dust to reduce the elements to the metallic state would be about 0.6 to 1 g/l. The rest was consumed by H_2 gas evolution:

$$H_2O + Zn \Rightarrow H_2 + Zn(OH)_2 \quad (35)$$

and residual metallic Zn in the final precipitate. The Zn powder consumption in this reaction could be from 5 to even 10 times the stoichiometric requirement for just precipitating the metals [27]. The Zn in the powder circulates internally in the plant, -through the electrolysis and back to the purification. Since the plant's zinc production is normally determined by the electrolysis, the recirculation will reduce the quantity of marketable zinc. With the cost structure of the plant, saved and sold powder will practically be charged only with the cost for raw material, and thus the profit margin would be the highest possible.

Besides consuming excess Zn dust, the H_2 evolution will also increase the pH, which can cause precipitation of $Zn(OH)_2$ (reaction 36), or more correctly basic Zn sulfates, $(Zn_x(SO_4)_y((OH)_2)_{(x-y)}$. Precipitation of these basic salts will finally render the surface of the metallic Zn powder passive and cause the cementation reaction to cease. If such a situation was not diagnosed correctly, more Zn powder would be added, causing the situation to worsen. Secondly, these basic salts show a very poor filterability, and could easily reduce the capacity of the filtration step considerably. At that time, the pH control by use of pH meters was not very reliable, mostly because of the flat correlation between pH and basicity of the plant solution. This caused frequently losses in production, both through process holdups and by impure solutions which reduced the current efficiency in the electrolysis.

Especially during the initial stage of the batch-operated Co removal step, the very poisonous arsine gas, AsH_3, was formed. This was especially pronounced when the first big shot of Zn powder was added to the reactor, but decreased then rapidly. This hazard was handled by using covered reactors equipped with effective ventilation. In the working area, problems with the arsine gas occurred if spill of Cu-precipitate came in contact with acidic solutions. As far as known all plants, which used this Co-removal technology, were operated in batch at that time.

3.2 Own development work on the Co removal

In the plant, this conventional method for Co-removal produced an unstable precipitate and re-dissolution of Co and also Ge occurred frequently during filtering and disturbances in the process operation. Especially, if the solution was too acidic, the re-dissolution rate increased considerably, and the pH control was a source for re-occurring interruptions in the plant operation. This seemingly easy trend to re-dissolve in acidic solution raised the question, if this harmful phenomenon instead could be utilized for Co and Ni recovery.

A process employing a circulating Cu-As precipitate as an activator in the removal step was envisioned. From the obtained precipitate, Co and Ni could be re-leached by an acid wash before the Cu precipitate was returned to the precipitation step as indicated in Fig, 16. Then the need for new Cu feed into the Co removal step might be substantially decreased, and it could be possible, even in plants with relatively low Cu in the raw solution, to remove most of the Cu as a pure product in a previous step. Preliminary experiments to clarify the possibility were made.

The approach failed, however, as both Co and Ni, on continuing re-circulation of the precipitate, ceased very quickly to be re-leached, and they seemed, on the contrary, to form very stable compounds. Electron microscopy (Micro-sond) investigations on the obtained precipitate revealed an element distribution, which seemed to indicate the occurrence of separate Co, Ni and Cu particles associated with As. Part of the Cu in the precipitate seemed also to appear in metallic form, whereas no metallic Co and Ni nor any identifiable mixed compounds of the tree metals were observed. The stoichiometric ratio of Me to As in these compounds indicated that they most probably were the arsenides CoAs, NiAs and Cu_3As. If so, the overall reactions taking place with Co and Ni had to be Eq. (36), and regarding Cu Eq. (37) and (38).

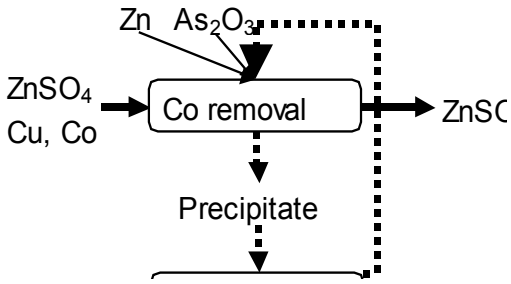


Fig. 16 Flowsheet based on an idea to improve Co removal.

$$Me^{2+} + AsO^{2-} + 2.5Zn + 2H_2O \Rightarrow MeAs + 2.5Zn^{2+} + 4OH^- \quad (36)$$

$$3Cu^{2+} + AsO^{2-} + 4.5Zn + 2H_2O \Rightarrow Cu_3As + 4.5Zn^{2+} + 4OH^- \quad (37)$$

$$Cu^{2+} + Zn \Rightarrow Cu + Zn \quad (38)$$

When these compounds occurred it was clear that:

- the role of As was not merely as an activator, but, as a stoichiometric reagent. It was also obvious that the precipitation, of these seemingly pure phases, must have taken place preferentially on the surface of their own specific arsenide crystals, especially as separate Co and Ni arsenides were formed in a precipitate with 60% Cu and only 1 to 2% of Co and Ni.

- in such a case, the precipitation rate should also be dependent on the quantity of active arsenide surface present.

Based on this assumption a new study was initiated with the aim to investigate whether a higher content of CoAs and NiAs seed present would improve the precipitation rates of the two metals. A second question was to clarify the role of Cu, especially as no compounds of Co and/or Ni associated with Cu were clearly visible. This could mean that a reduced demand for Cu could be possible. Not only could then most of the Cu be recovered in a preceding Cu precipitation step, but also, increased Co and Ni concentrations in the CoAs/NiAs precipitate could be achieved. This could offer possibilities for an economic recovery even of these very minor metals.

The above assumptions have later got support in the Master Thesis on the mechanism of the arsenic based Co removal by Ventin in 2001. Here was proved that Co cannot be reduced from $ZnSO_4$ solutions without the presence of an activating surface [28]. CoAs precipitated on Cu_3As and Cu cathodes but not on Pt. CoAs was not explicitly studied as a starting surface by Ventin, but as CoAs crystals could be identified by X-ray diffraction and SEM images on the activating surfaces, crystal growth had occurred, and this implicitly demonstrated that CoAs and NiAs surfaces acts as stronger activators than any other surfaces in the precipitate.

3.2.1 Experimental results

In the first series of batch experiments the produced precipitate was accumulated by passing it onwards from one experiment to the next. A brief description of this series is given in paper **[V]**. The results from this first series showed that the Zn powder consumption to reduce Co to less than 0.2 mg/l decreased drastically with increasing concentration of precipitate, and it was, at a seed concentration of only 5 g/l, far below the figures in the plant. The important feature was that Co and Ni could be precipitated even without any Cu^{2+} ions present in the solution, and that the seed material with a Cu-content of the same level as the combined Co and Ni was working very satisfactory. These first experiments showed that the problems encountered with the grade of the Cu precipitate could largely be solved with this new procedure. With the Cu, Co and Ni concentrations in the plant solution, only 5 to 10% of the Cu would be needed in the Co removal and the rest could be precipitated as a clean product in a preceding step.

As the Co removal in the plant was operated in batch and the mechanical performance of the new system was very much the same as the old one, a long-time experiment on production scale was initiated. Minor changes, to ensure the retention of sufficient seed material, were done on one reactor, and this was then put into operation. Laboratory studies were also continued to clarify the chemistry in more detail. The most important results of this work, concerning both the process chemistry and the influence on the plant operation, are given in papers and patents **V - VII**.

The first experimental series, reported in **V**, showed that Cu^{2+} could be left out from the feed solution for a number of batches with still continuing precipitation of Co. The same was tested for As_2O_3, and even with a similar result. For both additions this was, however, valid only for a number of consecutive experiments, after which the precipitation declined and virtually ceased.

The laboratory studies and the operation of the production scale reactor in the plant demonstrated that

- the precipitation rates increased with increasing concentration of the precipitate simultaneously with significant decrease in Zn powder consumption, which approached the equivalent demand.
- the amount of Cu^{2+} in the start solution could be decreased to a fraction of the earlier recommended and used, but, only to a certain level, which could be about the same as the sum of Co and Ni. Further reduction of Cu^{2+} changed the physical appearance of the precipitate; from forming big flocks, resulting in rapid settling of the solid and a completely clear overflow solution, disintegrated into finely divided slurry that did not settle. At this stage, the precipitation of Co and Ni ceased almost completely.
- when leaving out the addition of As_2O_3 (to investigate the sensitivity to process disturbances), the precipitation continued as normal for three to five batches, but the precipitation rate decreased then rapidly.
- if As addition exceeded the quantity needed to form arsenides with all metals, CoAs, NiAs and Cu_3As, the flocks also disintegrated, and the effect was the same as with too low Cu.
- the low Zn powder consumption came from substantially reduced H_2 gas evolution, resulting in a substantially lower increase in pH. This stabilized the operation as intermediate pH corrections were not necessary during the batch precipitation.
- re-dissolution of the precipitate at lower pH did not occur any longer.

On the basis of these observations a model of the system, visualized in Fig. 17, was assumed to be:

- all As reacts with Co, Ni and Cu according to reactions (36) and (37) to form separate arsenide crystals. With a suitable under-stoichiometric amount of As, part of the Cu will be precipitated in metallic form, Eq. (38).

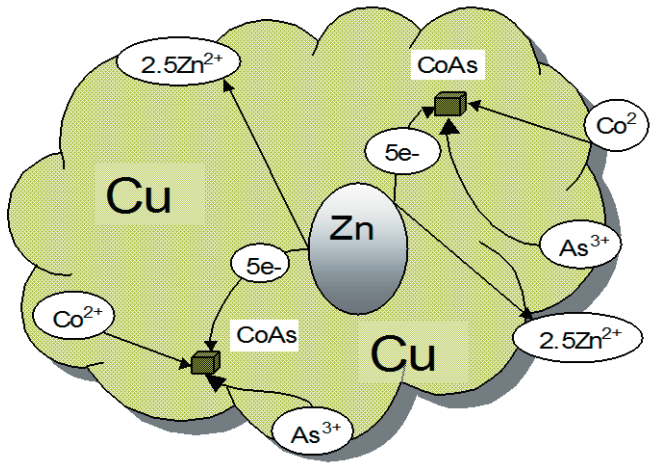


Fig.17. Conceptual model of the chemistry in the Co removal.

- the very strong influence of the physical appearance of the precipitate on the rate of precipitation seemed to be dependent on the state of Cu in the precipitate. The flocculated state of the precipitate seemed to occur when metallic Cu was present, and this appeared to be the key to both higher precipitation rates and suppressed Zn powder demand.
- it was supposed that metallic Cu in the flocculated precipitate provided an electrically conductive path between the Zn dust particles and the Me arsenide particles. This implied that the electrons could move freely in a large space of the precipitate around the Zn particle, and no direct contact between the metallic Zn and the arsenides was needed.

To operate this process in plant scale, the precipitation should then take place in the presence of high concentrations of precipitated seed particles of metal arsenides and dispersed Zn powder in a fluidized or agitated bed of flocculated and electrically conducting material. As the Co removal in the plant was operated batchwise, only small changes to the reactors to allow for the retention of a sufficient quantity of seed were needed to adopt the new process.

After the process was tested in a full-scale batch reactor in the plant, it was shortly adopted for the whole production line [**V - IX**].
When the plant capacity was expanded in 1974, substantially improved processes for separate Cu- and Cd-removal steps were also added, and the system was operated as illustrated in Fig. 18. The main paths for the elements removed are also given in the flowsheet.

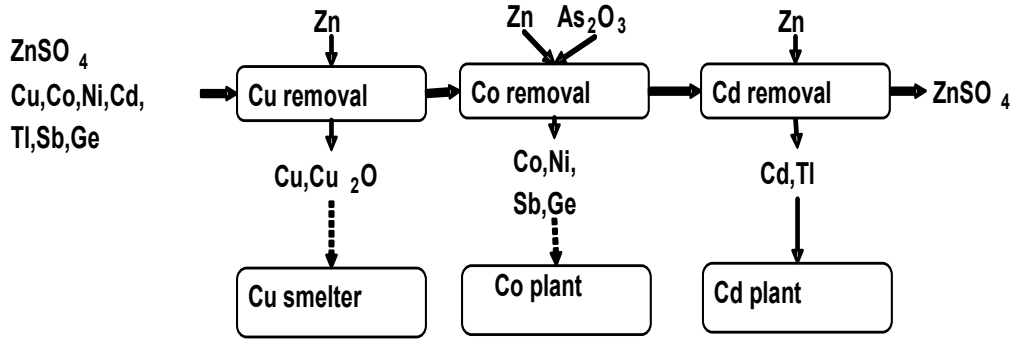


Fig. 18. Flowsheet of the Outokumpu purification process.

3.2.2. About the chemistry of Co removal

According to the above model, the oxidation, or anodic reaction, takes place on the Zn surface:

$$2.5Zn \Rightarrow 2.5Zn^{2+} + 5e- \quad (39)$$

and the electrons pass through the copper bed to the arsenide particles where the reduction, - the cathodic reaction ,- takes place:

$$5e- + Me^{2+} + As^{3+} \Rightarrow MeAs \quad (40)$$

With a high concentration of arsenide surface in the bed, the reducing power of the Zn particle is acting over a much larger cathodic surface area than the area on the Zn particle itself, and hence the cathodic current density can be maintained much lower than the anodic one. If the cathodic current density is maintained sufficiently low, by keeping a low concentration of Zn powder in the bed, the reduction of the different metal species will take place successively according to their stability, or the purification act as a potentiometric titration. Sufficiently low cathodic current means that the anodic current should be balanced by the diffusion of metal ions to the cathodic arsenide surfaces.
At the start of a batch, as the concentration of metal ions is high, the balance is easier to reach and the selectivity between the metals can be obtained even at relatively high exchange current densities. As H_2 gas evolution has not been

noticed during this time it indicates that the anodic current is well balanced by the diffusion of metal ions, or, that H_2 evolution is prevented by a high over potential, or simply by H_2 being less stable than the precipitates formed. With metallic Cu in the precipitate, on which the hydrogen over potential is low, the possibility for H_2 gas evolution should be good. When this is not taking place, the conclusion can be drawn that the formed metal compounds are more stable than H_2 gas. Hydrogen formation should than start first when the metal ion concentration is too low to balance the anodic current, or, towards the end of the purification.

A low cathodic current density will provide a good selectivity between the precipitated species, and it is also reasonable to assume that the result will be more perfect crystal growth and hence more stable precipitates will be obtained. This can be an explanation for the good stability of the solids against acid, as was observed both in laboratory-scale experiments and plant operation.

Fig. 19 shows a picture from an internal Outotec report 2005 by Honkala reveals the element distribution in a Co-precipitate from the plant [29].

The two big particles on the image are secondary agglomerates of individual particles with diameter less than 1 μm. The aim of this study for which this image was recorded, was to clarify the mechanism behind this undesirable agglomeration which had caused process disturbances.

During the agglomeration, a separation of the individual metal species into concentrated zones has occurred. A close examination reveals areas with relative over-representation of each of the four main elements Cu, Co, Ni and As, as well as the minor impurities Sb, Ge and Te.

It is evident that Co and Ni are always associated with As, whereas Cu occur both together with As and alone. Sb and Ge are both more closely related to Ni than to Cu and Co, but the compounds formed from these two elements were not identified. Tellurium, which is normally not monitored during the purification, shows no association with any specific element, but seems to be evenly distributed over all phases. Al and Si, which presumably occur as $Al(OH)_3$ respective SiO_2 gel and/or silicates, might have played a role in the agglomeration which took place. Basic sulfates or/and silicates are probably explaining the occurrence of zinc within the agglomerate. Washing had probably been too fast and/or pH too high to remove these Zn compounds from inside the agglomerates during the sample preparation. The surface of the agglomerates is also covered by a layer of $Al(OH)_3$ and SiO_2, which indicates that the agglomerates are not formed during the sample preparation. The solid in the slurry sample represents about 50 times the amount precipitated per

purification loop and there would not be enough Al^{3+} and soluble silica in a sample solution to build up such a thick layer. Accordingly the agglomerates must have been formed in the plant, and their influence on the precipitation rates were strongly retarding.

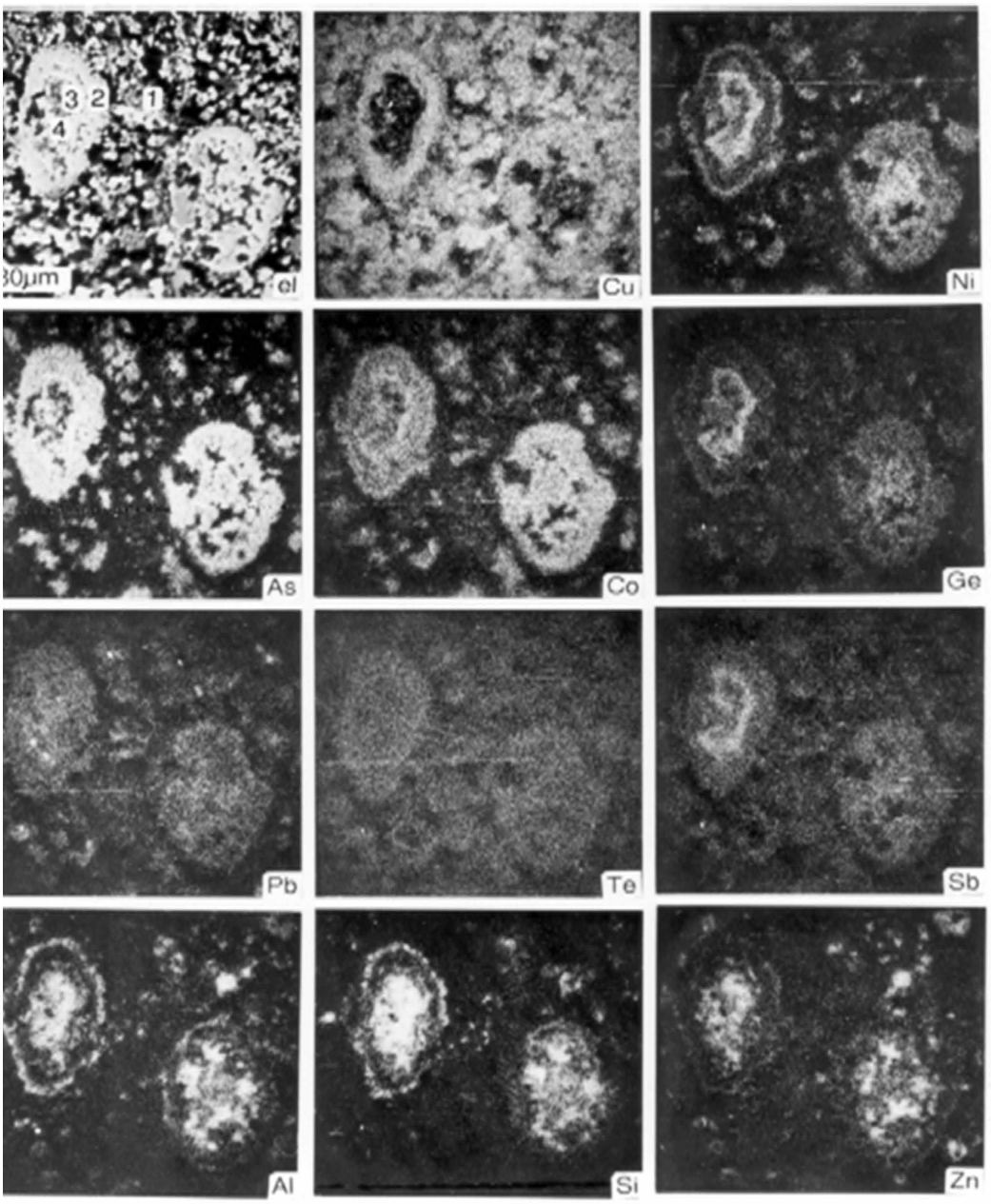


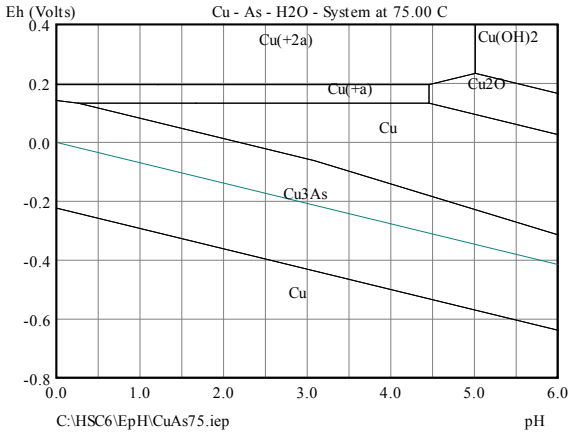
Fig. 19. SEM image showing element distribution in a Co removal precipitate from the plant.

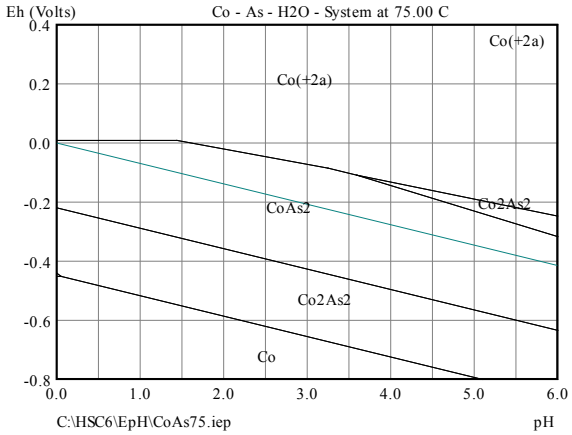
3.2.3 Thermodynamic calculations on As based Co removal

To clarify the conformity between the observations made from Fig. 19 and the conclusions drawn above from the experimental results, the thermodynamics of the system has been examined through calculations with the Eh - pH and Equilibrium Calculation modules of the HSC6 Chemistry program [20]. In the first calculations, all major compounds that according to the HSC database can possibly form in this system were included in the calculations.

The three first Eh-pH diagrams, Fig 20. show the stability areas for the Me/As compounds for the major elements Cu, Co and Ni and at 75 °C. Eh between 0.4 and -0.8 V and pH from 0 to 6. Element molalities were $10^{\wedge -5}$ mol/kg.

In the three following graphs, Fig 21, the most stable compounds of Te, Ge, and Sb form with the metals are shown. Molalities of the elements were $10^{\wedge -6}$ mol/kg.





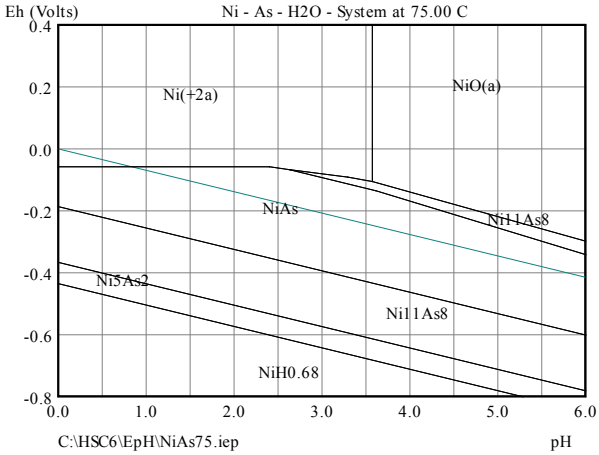


Fig. 20. Stability areas for Cu, Co and Ni arsenides at element concentrations of $10^{\wedge -6}$ mol/kg.

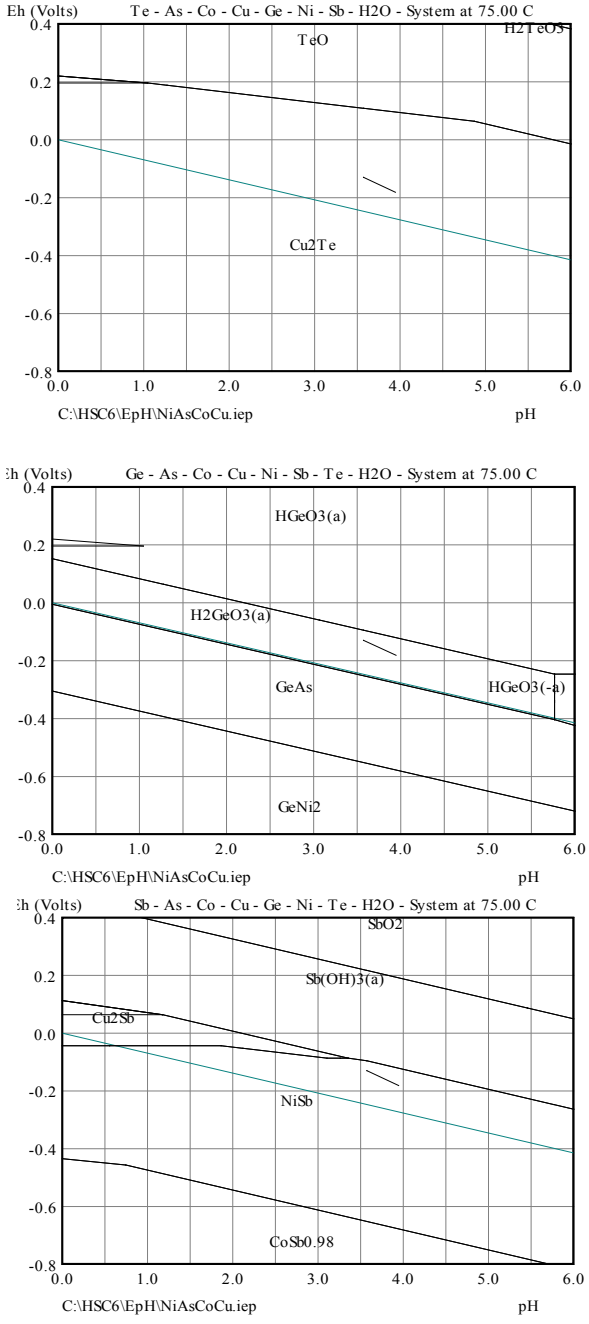


Fig. 21. Stability areas for different compounds Te, Sb and Ge can form with Cu, Ni, Co and As in the Co removal at element concentrations of 10^{-6} mol/kg.

The diagrams in Fig. 20 show that on reduction at pH below 3, the most stable phases of the three major elements are metallic Cu followed by Cu_3As, NiAs and $CoAs_2$, whereas at the normal pH of 4 to 5 in the Co removal, $Ni_{11}As_8$ and Co_2As_2 are the most stable Ni respectively Co compounds. With further reduction, other arsenides are formed, and even metallic Cu will reappear.

Fig. 21 show that Cu_2Te is even more stable than Cu, and Te should be the first element to precipitate. Even TeO shows up as a solid phase at a concentration of only 10^{-6} mol/kg. Both of these compounds could explain the more homogeneous distribution of Te in the sample in Fig.19. The most stable Ge phase is GeAs, but on further reduction, $GeNi_2$ is formed. This might explain the likewise in Fig.19 observed relation between Ge and Ni. Sb will at pH 2 -5 form NiSb, which supports the observation from Fig.19 that Sb is more related to Ni than to Cu and Co.

The progress of a Co removal batch as a function of reacted Zn powder was calculated with the Equilibrium Compositions module of HSC 6.1. The metal concentrations in the starting solution were about 40 to 70 mg/l and As in a quantity to give both Cu and Cu_3As in the final precipitate. The solution contained 2.5 mol/l $ZnSO_4$.

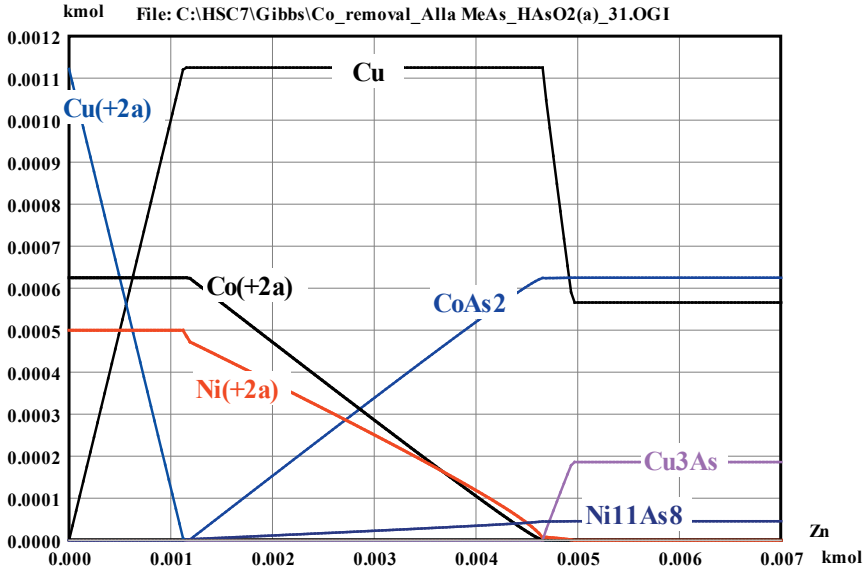


Fig.22. Thermodynamically stable phases formed in the Co removal as function of Zn addition. All Co/Ni arsenides compounds considered.

The same compounds as in the calculations of the Eh-pH diagrams for the individual elements were included in these calculations, too. The relative stability and order of formation of the different species are shown in Fig 22.

According to the diagram, Co and Ni should precipitate simultaneously, whereas experimentally it has always been found that Ni precipitates first, and even with a marked selectivity over Co. A typical example is shown in Fig. 23. In this experiment, very high concentrations of both Ni^{2+} and Co^{2+} were precipitated. Since selectivity was not strived for, a stoichiometric amount of Zn powder to precipitate all three metals was added in one shot at the start of the precipitation, and still a rather good selectivity was achieved. This experiment shows also that the precipitation of Ni and Co proceeds with a Cu content less than the sum of Co + Ni in solution.

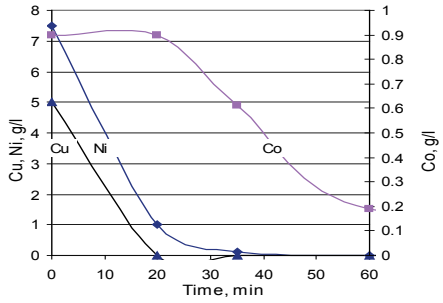


Fig. 23. Normal experimentally obtained selectivity between Co and Ni.

The discrepancy concerning the precipitation order of Co and Ni is probably related to kinetics. The nucleation and formation of a complex compound such as $Ni_{11}As_8$ is probably slower than for NiAs, and likewise for $CoAs_2$ and Co_2As_2 versus CoAs.

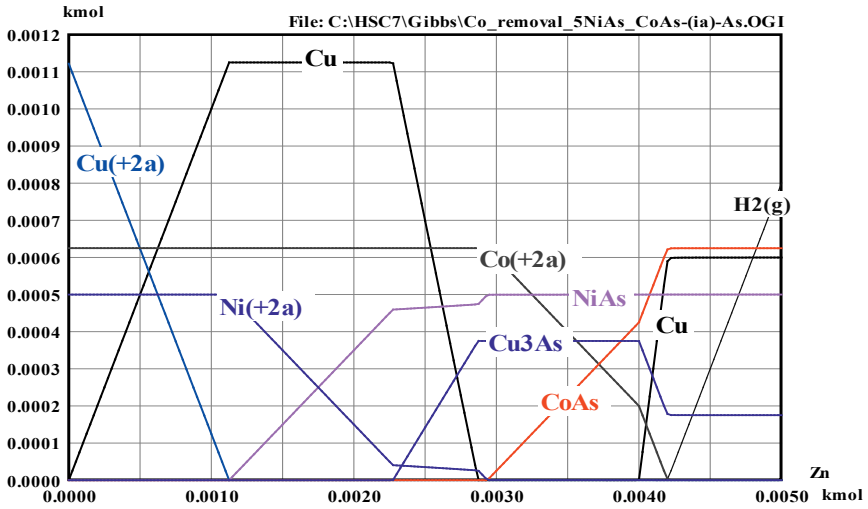


Fig.24. Thermodynamically stable phases formed in the Co removal as function of Zn addition. Only CoAs and NiAs considered.

A calculation with only NiAs and CoAs considered as stable phases, shown in Fig. 24, reveals that now NiAs is precipitated before CoAs. The selectivity between Ni and Co is also in conformity with the results obtained in precipitation experiments, (Fig. 23), and supports the assumption about a kinetic effect.

Fig. 22 and 24 reveal that the major part of added As_2O_3 should precipitate as, $Co(AsO_2)_2$, which would be the main source of As during the precipitation. When $Co(AsO_2)_2$ is consumed, Cu_3As serve as the As source for remaining elements in solution:

$$Cu_3As + Co^{2+} + Zn = CoAs + 3Cu + Zn^{2+} \quad \Delta G\ -136\ kJ/mol \quad \log K = 22 \quad (41)$$

In practice, the final ratio of Cu to Cu_3As in the precipitate is determined by the quantity of As added over the stoichiometric demand of Co and Ni and other arsenides forming elements. The other elements, Sb and Ge and Te, of which only Ge seems to form arsenide, appear in very low concentrations in the actual process solutions, and they do not notably influence on the need for As. In practice, the concentrations of Co^{2+}, Ni^{2+} and a suitable ratio of Cu_3As to (Co,Ni)As in the precipitate will determine the need for As_2O_3.

Fig. 25 shows the stable phases for Sb, Ge and Te being NiSb, GeAs and CuTe. GeAs is the least stable phase and thus the last solid phase to precipitate, after which hydrogen evolution will dominate.

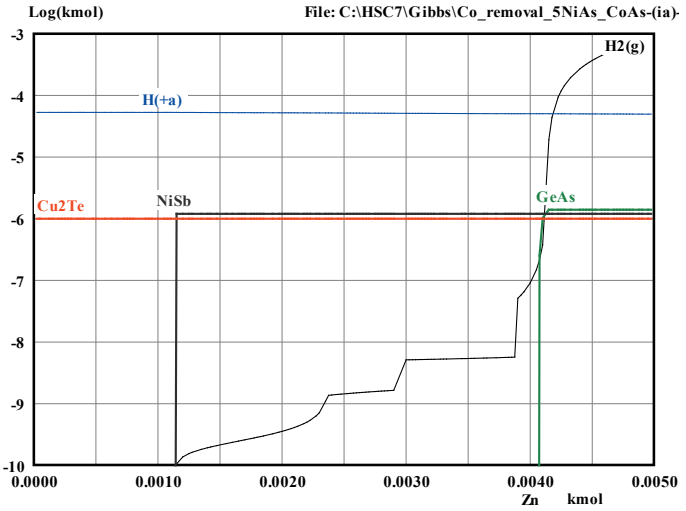


Fig. 25 Stable phases of Te, Sb and Ge.

In Fig. 26 the stability of H_2 gas and the gaseous hydrides reveal two important features, which are explained below:

1. First, significant amounts of H_2 gas should not evolve until all impurities have been precipitated. This implies that all impurities are precipitated into compounds that are thermo-dynamically stable in an oxygen-free plant solution at the normal pH of around 4 to 5. Accordingly, even without metallic Zn present in the precipitate, no or very minor re-

dissolution will take place. This has been observed both in laboratory experiments and during plant operation and it is of great importance for the stability and reliability of the industrial process.

2. Second, thermodynamically the concentration of arsine gas, AsH_3, in the reactor should be very low; only about 10^{-10} times the concentration of hydrogen gas. If H_2 gas is controlled to 1% in the ventilation air from the reactors, arsine gas will not be a problem.

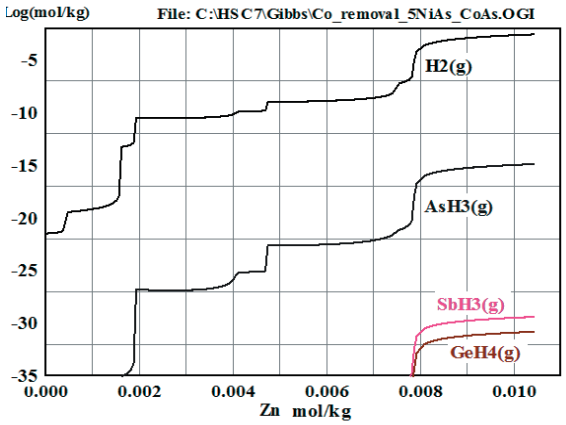


Fig. 26 Stability of hydride producing phases during acidification of Co removal residue.

In addition, because the precipitate does not contain any metallic zinc, no AsH_3 gas will be formed even in acidic solutions. This used to be the major hazard with the old system when spills of precipitate came in contact with acidic solutions in the workplace area.

Results from a calculation on acid addition to final slurry of precipitate (NiAs, CoAs Cu_3As, Cu, Cu_2Te, GeAs and NiSb) given in Fig. 27 show negligible equilibrium concentrations of AsH_3 gas even at very high acid concentrations.

Fig. 27 shows also that the solubility of CoAs is increasing with the acid concentration (as it should be according to equation (37). Neither in laboratory nor in the plant was, however, observed any difficulties in reaching lower concentrations of Co^{2+} than 0.2 mg/l that could be attributed to low pH.

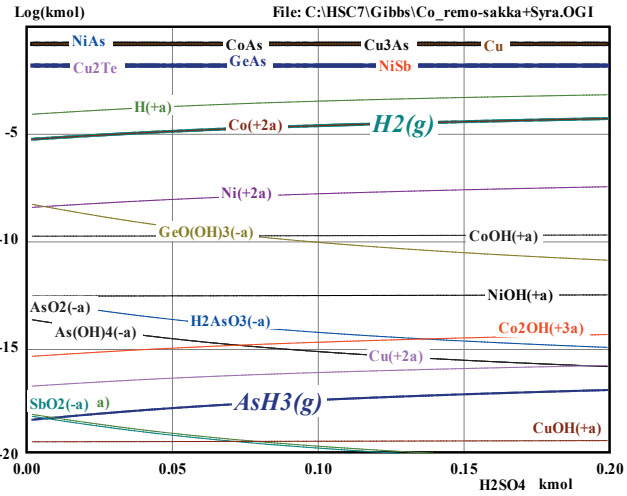


Fig. 27 Addition of acid to final residue.

Results of calculations on the magnitude of a possible pH influence (or rather acid concentration in the start solution) on the Co removal are given in Fig. 28.

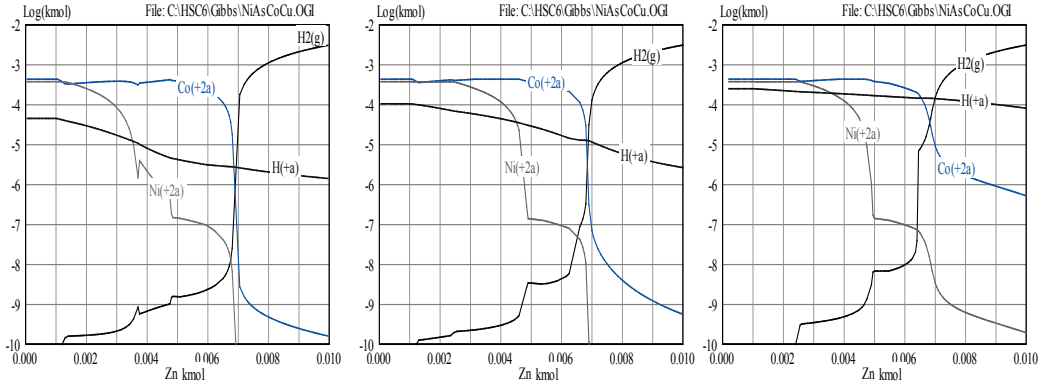


Fig. 28. Influence of initial acid concentration on Co removal. From left 0, 0.3, and 1 g/l H_2SO_4. Initial Co^{2+}, Ni^{2+} and Cu^{2+} concentrations 0.001, 0.0008 and 0.002 mol/l respectively. 75 °C.

The calculations show that the acid concentration should have a clear effect. Normal operation in the Co removal is, however, to keep the pH as high as possible, as in the left diagram, and thus the effect of pH/acid would not be easily noticed. Any published studies on the influence of pH have not been found in the literature.

3.2.4 Discussion on the Co-removal

The thermodynamic calculations above support the process model in Fig. 17, which was envisioned from the experimental results obtained during the development of the process:

- The role of As is to precipitate the metals as arsenides, which most probably are Cu_3As, CoAs and NiAs.
- The arsenides provide activating surfaces for the precipitation of the individual metals.
- Cu_3As in the bed will provide As for Co and Ni precipitation if addition of As_2O_3 is interrupted.
- All removed metal-impurities form compounds more noble than H_2 gas, and thus substantial quantities of H_2 will not evolve as long as the anodic current from the metallic zinc is lower than the limiting cathodic current from diffusion of impurity ions to the arsenide surfaces. This support the hypothesis that an electrically conducting path between the Zn powder particle and the arsenide particles, which greatly expand the cathode surface, is a vital factor in reducing the H_2 gas evolution, and thereby Zn powder consumption. It is reasonable to assume that this path is provided by the flocculated metallic copper.

The principles of the plant operation based on this acquired new knowledge of the chemistry can be summarized as follows:

- Sufficient precipitate should be retained in the system to provide sufficiently high precipitation rates. The bed of precipitate should contain enough Cu_3As to provide an As buffer for a reasonably long period of time and sufficient metallic Cu to provide flocculation and conductivity of the bed.
- A content of Cu equal to the sum of Co and Ni divided equally between Cu_3As and metallic Cu in the precipitate has experimentally proved to provide good operational performance. Due to normally low and stable Cu, Co and Ni concentrations in the feed solution to the Co removal and good settling properties of the precipitate, it is easy to accumulate an amount of circulating precipitate that assure an As buffer for well over one day's need. The composition of the precipitate, which is adjusted by the As_2O_3 addition, can than be controlled by just one daily Co, Ni, Cu and As analyze of the precipitate.

To minimize the H_2 evolution, the Zn powder addition should as close as possible balance the rate of diffusion of the metal ions to the active sites in the

bed. This implies that the feed rate of Zn powder should be a function of the remaining metal ion concentration.

As the precipitation is a redox reaction, the Zn powder feed can be controlled by the redox potential of the bed. As also the H_2 formation is low, the addition of As_2O_3 and the acid for pH adjustment can be steered by simple proportional and the set point controlled by a daily titration of the acidity of the solution as a control of the pH measurement.

This new process was for many years operated in batch at the Kokkola plant. The thermodynamic calculations with HSC in Fig. 29 are also in good agreement with observations made during plant operation. When the solution was fed to the slurry of precipitate left on the bottom of the reactor before Zn powder addition was started, Cu^{2+} while the Co^{2+} and Ge^{n+} concentrations in the solution increased. This is a result of the oxidation of the least stable phases in the precipitate, CoAs and GeAs, by Cu^{2+} ions in the feed solution.

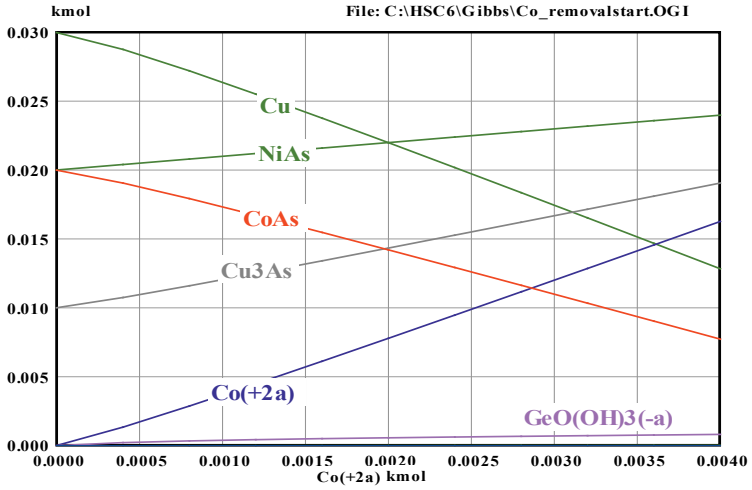


Fig. 29. Slurry of Me_xAs_y is "titrated" with Co, Ni, and Cu sulfate in proportion 1:1:2. CoAs and GeAs are dissolved, and their As form NiAs and Cu_3As with Cu^{2+} and Cu metal.

Fig. 29 reveals that CoAs should be oxidized to Co^{2+} and AsO_2^- while Cu^{2+} is reduced to the metallic state, which is the most stable Cu phase at the start of reduction of the impure solution. An increase in the Ni^{2+} concentration was not noticed due to the high concentration of CoAs in the solid compared to the Cu^{2+} quantity in the incoming solution. Reaction (43) explains thus the precipitation of Cu^{2+} without metallic Zn.

The conclusion drawn from Fig. 17, is that Cu, Co and Ni do not form mixed compounds, but separate arsenide phases can also be anticipated from the different crystal structures of the three compounds;- cubic for Cu_3As, hexagonal for CoAs and orthorhombic for NiAs [30].

3.2.5 Comparison of the As and the Sb based purifications

A summary of the extensive research work done on the mechanisms of the Sb/Cu based cobalt purification is given here.

The need for Sb is very low; a molar ratio of Sb/Co even as low as1/50 can be sufficient. It is regard that Cu and Sb form first a substrate on the surface of the Zn powder, on which Co precipitates in an alloy with Zn and Cu and Sb. If present in the solution also Cd will precipitate into the alloy. It is also shown that the alloy, judging from the SEM micrographs, is precipitated as a layer on the surface of the zinc particle. This layer seems to loosen from the zinc surface at the end of the precipitation. The composition of the alloy varies with the quantities of Cu and Cd in solution, and even with temperature [31-34].

Thus the crucial feature of the As-process, that Co and Ni precipitate as chemical compounds which do not need any direct contact with the metallic Zn surface seems to be lacking from the Sb activated system. If a direct contact with the metallic Zn is always required for the precipitation reaction in the Sb-activated process to proceed, the “precipitating surface” will be much smaller than that in the As-based process described in this work. The volumetric precipitation rate will then be much lower, and to compensate for this more and fine Zn powder or longer retention time is needed.

Thermodynamic data for alloys precipitated with Sb as an activator or testing of their stability in process solution have not been found in the literature. Boyanov *et al*. [35] have; however, in experiments with Sb noticed that re-dissolution of impurities will start on long retention times, which indicate that the precipitate in question was not thermodynamically stable in the solution without any contact with metallic Zn.

The formation of AsH_3 gas, which has been the main cause for the adoption of the Sb process, was in the old As process very strong during the initial stage of the batch. This was most probably caused by high Zn powder load to a solution with practically no activating precipitate present. With that procedure poor selectivity was obtained, and all thermodynamically possible reactions including H_2 and AsH_3 gas formation, could take place simultaneously on the Zn powder surface. When the new process was first adopted in the old batch

reactors in the Kokkola plant, the AsH_3 gas evolution decreased by about 80 to 85%, and when a new continuous system was introduced practically no AsH_3 gas was developing.

The most severe work-place hazard occurred, however, through generated arsine gas in the working area when spilling of final residue, which contained metallic Zn, came in contact with acidic solutions outside the reactors:

$$2CoAs + 3H_2SO_4 + Zn = 2Co^{2+} + 2AsH_3 + Zn^{2+} + 3SO_4^{2-} \quad \Delta G = -36 \text{ kcal/mol} \quad (42)$$

In the new process, with no need for metallic Zn to be present in the final residue, AsH_3 should not form. Confirmation on this has been obtained from the present Boliden plant in Kokkola, where no difficulties with AsH_3 formation have occurred since continuous operation of the step was introduced [private communication].

3.3. Copper removal

With introduction of the new Co removal less than 100 mg/l of Cu^{2+} was needed in the feed solution. This meant that 80 to 95% of the Cu in solution could be precipitated selectively in a preceding Cu removal step. Even though the As content in the Cu precipitate might be low, Cd would still be a concern in the copper smelter. Zinc plants, having a primary Cu removal, normally reported a Cd content of 2 to 3% in the precipitate, and even in an overview paper on and for the zinc industry published by Yamada (not public report) as late as in 1985, the Cd contents in Cu precipitates were reported to still be in the 1 to 3% range. These numbers imply that 1000 t/a of such Cu material would stand for most of the Cd intake to an average copper smelter.

Studies, to investigate whether Cd could be re-leached from the Cu precipitate by an acid leach under H_2 gas evolution, showed, however, that this was not the case, as a big part of the Cd was left un-dissolved. This Cd could only be leached with oxidation and simultaneous leaching also of Cu. This was taken as an indication that this part of the Cd did not occur as a separate phase, but in an alloy with Cu.

The data given in the HSC program on two Cu/Cd alloys, Cu_2Cd and Cu_4Cd_3, show that they should react to Cu^0, Cd^{2+} and H_2 gas even at a rather high pH:

$$Cu_2Cd + 2H^+ = Cd^{2+} + 2Cu + H_2 \qquad K = 7.5*10^{11} \qquad (42)$$

This reaction was, however, not observed in the mentioned leach experiments, which either is due to very slow kinetics, or that these phases are imbedded in

the metallic Cu phase and not easily accessible to the acid, or, that more Cu rich, and more stable, phases than the two ones mentioned had been formed.

Normally the Zn plant solutions contain Cu about one to three times the quantity of Cd, and consequently the 1 to 3% Cd in the Cu product show, nevertheless, that still a substantial selectivity is achieved. It was then assumed that this selectivity could possibly be improved upon by the same means as in the Co removal, or that the precipitation should take place in an electrically conducting bed of the Cu precipitate at a low cathodic exchange current density.

This concept was tested by batch experiments in bench scale, and the results showed that the presence of a bed of metallic Cu would considerably reduce the co-precipitation of Cd. It showed also that the Cu precipitate flocculated and settled at a rate that could allow the use of fluidized bed operation. This was consequently tested on a pilot scale. Except for avoiding Cd precipitation, a second main objective of the Cu removal was to satisfy the need for Cu to the succeeding Co removal step, or an amount about equal to the sum of the Co + Ni contents of the solution. With the concentration of these two metals in the plant solution, this leads to 25 to 100 mg/l Cu^{2+} in the final solution.

In a fluidized bed, this gives a slurry of metallic Cu precipitate present in a solution containing Cu^{2+} ions, and the simple cementation reaction:

$$Cu^{2+} + Zn \Rightarrow Cu + Zn^{2+} \tag{43}$$

will, at the pH of a normal “neutral solution” be competing with the precipitation of cuprous oxide, Cu_2O:

$$Cu^{2+} + Cu + H_2O \Rightarrow Cu_2O + 2H^{+} \tag{44}$$

This reduces Zn powder consumption, but it had also an adverse effect on the flocculation of the precipitate. As long as the precipitate consisted of metallic copper only, the whole precipitate formed big flocks like in the Co removal, and the solid settled readily. The formed cuprous oxide did, however, not flocculate, and the Cu_2O was “washed” out of the fluidized bed reactor and ended up in the Co removal. The development on a normal fluidized bed system was then abandoned in favor of back mixed reactors, and such a system was introduced in the plant.

To maintain a bed of precipitate in the reactors, the final slurry was run through a settler and the underflow was recycled back to the first reactor. By this system, the Cd content of the Cu cake could be reduced down to even 0.1% in plant operation.

Cuprous oxide was, though, a physical nuisance in this system, as a part of it reported to the thickener overflow which was fed to the Co removal which leads to a dilution of the Co precipitate. This decreases its value as a feed for Co production. This dilution of the Co precipitate could easily have been avoided by having a filtration of the overflow from the thickener after the Cu removal.

Both metallic Cu and Cu_2O are favorable feeds to a Cu smelter. The capacity of a flash smelter is dependent on both gas volume and cooling capacity, and these compounds will influence favorably on both parameters. This is seen from the three smelting reaction equations at 1200 °C with:

1) concentrate, $CuFeS_2$, alone Eq. (45)

2) and 3) concentrate and addition of Cu respective Cu_2O, Eq. (46) and (47):

$$2CuFeS_2 + 4O_{2(g)} = Cu_2S + 2FeO + 3SO_{2(g)} \quad \Delta H \approx -292\text{kcal/mol} \qquad (45)$$

$$2CuFeS_2 + 3O_{2(g)} + 2Cu = 2Cu_2S + 2FeO + 2SO_{2(g)} \quad \Delta H \approx -241\ \text{kcal/mol} \qquad (46)$$

$$2CuFeS_2 + 2.5O_{2(g)} + Cu_2O = 2Cu_2S + 2FeO + 2SO_{2(g)} \quad \Delta H \approx -195\ \text{kcal/mol} \qquad (47)$$

The reactions show that Cu_2O, due to the highest cooling effect and the lowest oxygen demand, is the most favorable component. The lesser heat evolved can be used for smelting of additional concentrates, and thus the smelting of the "Cu-cake" will not tie up any capacity for concentrate smelting, but instead increase it by about 2/3 mol of $CuFeS_2$ for each mol Cu_2O added. Accordingly, precipitation of Cu_2O could be the most favorable alternative both for the Zn plant and the Cu smelter with regard to the capacity of both plants.

3.3.1. Thermodynamics in the Cu removal

The results from equilibrium calculations on batch-operated Cu precipitation as a function of Zn powder addition are shown in Fig 30. The solid phases considered are Cu, Cu_2O, Cu_2Cd, Cu_4Cd_3, Cd, $Zn(OH)_2$, $Cd(OH)_2$ and $Cu(OH)_2$.

Fig. 35 shows that the Cu/Cd species included in the calculation are not precipitated, and thus not stable in the process solution, and consequently the H_2 gas evolution starts after Cu is removed. The high H_2 gas overpotential on Cd enables, however, Cd to be precipitated, and if H_2 gas evolution is left out from the calculation, Cu-Cd species precipitate, but, first after Cu is removed.

That Cd has been found in Cu precipitate even though the Cu^{2+} concentration has been about 100 mg/l means, that the anodic current has exceeded the current from diffusion of Cu^{2+} and H^{+} ions to the cathode surface.

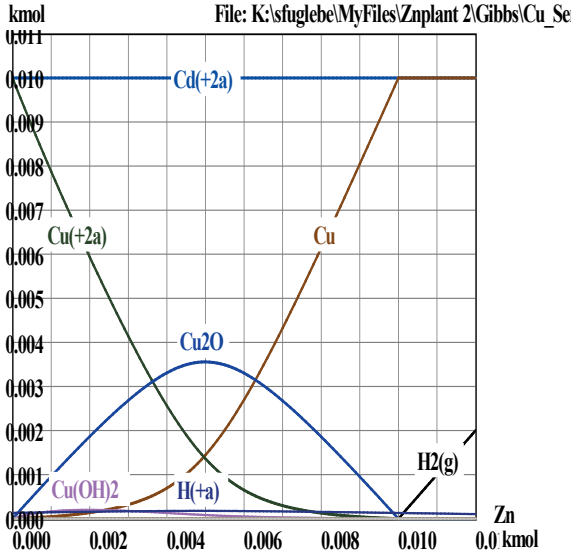


Fig. 30. Cementation of Cu^{2+} and Cd^{2+} by Zn. H_2 gas allowed.

Accordingly, the same means used to increase the selectivity in the Co removal should also minimize the co-precipitation of Cd in the Cu removal, or, use of a fluidized bed and balancing the cathodic and anodic exchange currents with the Zn powder addition. With the aim to have an outgoing Cu^{2+} concentration of 50 mg/l (≈0.0008 mol/l) in the solution and a possibly high Cu_2O content in the solid, the Zn powder addition should according to the calculations be about 60% of the stoichiometric needed to precipitate all Cu in metallic form. As the main target would be the final Cu^{2+} concentration, the process control should be based on its frequent analyses.

3.4. Cd removal

3.4.1. Introduction

The only noticeable impurities left in the solution after the Co removal are Cd and Tl, and these elements are removed in the last step through cementation with Zn powder only:

$$CdSO_4 + Zn \Rightarrow Cd + ZnSO_4 \quad (48)$$

As frequent in cementation reactions, Cd forms very easily a dendritic precipitate, which is broken off from the surface of the Zn powder particle. When, however, the contact with the metallic Zn is lost, Cd will, despite its high overpotential, react with H_2O and slowly re-dissolve under H_2 gas evolution:

$$Cd + H_2O \Rightarrow Cd^{2+} + 2OH^- + H_2 \qquad K = 5*10^{11} \quad (49)$$

Even though the stability of Cd slightly increases with the temperature, the reaction rate, Eq. (49), is favored by high temperature, probably through easier bubble formation at higher vapor pressure. With the high specific surface area of the dendrites, the Cd^{2+} concentration in the solution very quickly exceeds the maximum of 1 mg/l, which is needed to keep the Cd content in the produced Zn within specifications. To cope with this re-dissolution tendency and to reach reasonable retention times of 1.5 and 2 hours for, a 5 to 10 times stoichiometric amount of Zn dust was normally used in plant operation. The high surplus of Zn powder resulted also in a precipitate, “Cd cake”, containing about 60% of Zn, of which a big part was metallic, and only 15 to 20% of Cd. In the Cd plant, this precipitate was leached in spent Zn electrolyte, and more than 80% of the solution flow was needed for leaching of Zn. Thus the equipment and the investment cost in the Cd plant were to a major part determined by the Zn content in the precipitate. Hence costs for the high demand of Zn powder in the purification were induced both through losses in Zn production and from high investment costs for the Cd plant.

To improve the Cd precipitation, systems based on fluidized and agitated bed principles were under development [36-38]. Besides to achieve high volumetric precipitation rates, these systems aimed also at peeling off the dendritic Cd product from the Zn surface to produce a high-grade Cd precipitate, and thus maintain a high precipitation rate on the Zn powder surface until complete consumption of the Zn particle was achieved.

3.4.2. Development of a new Cd removal

Own bench scale experiments, where the Zn bed was fluidized only by the upward flow of solution, showed that the bed agglomerated in a very early stage, and that fluidization could not be kept for any longer period of time. Experiments at 70 °C in a batch reactor, provided with mechanical agitation for the dispersion of the bed, were then undertaken. Continuous flow was simulated by pumping a small volume of a 300 g/l Cd containing solution continuously into the reactor. During experiments, where the influence of agitation was studied, it was noted that with vigorous agitation, hardly any peel-off of precipitated Cd from the Zn powder surface occurred.

Photographs of the obtained precipitate as such, and on a polished specimen are shown in Fig. 31. The pictures demonstrate that Cd has precipitated as a crust onto the Zn particles and the metallic zinc had corroded away from underneath this crust.

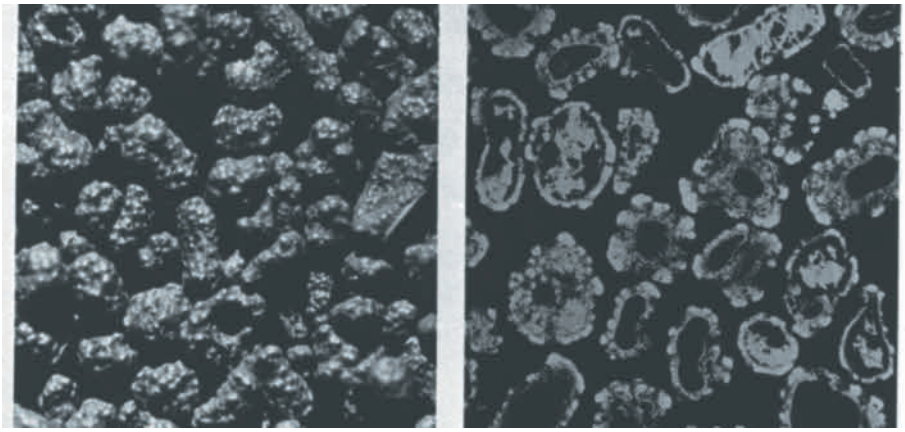


Fig. 31. Photographs of Cd precipitate produced in a fluidized bed of Zn powder.
Left: the precipitate as such. Right: polished specimen.

Experiments to study the influence of this crust on the precipitation rate were performed in the same reactor. A plant solution taken after the Co removal and a batch of Zn dust with a grain size distribution from 150 to 250 µm was added. A concentrated $CdSO_4$ solution (300g/l Cd) was pumped into the reactor at a rate that should consume the Zn powder in about 24 h. Cadmium in solution and solid were analyzed at 2 hour intervals, and the results are given in Fig. 32 as Cd^{2+} as a function of Cd in the solid.

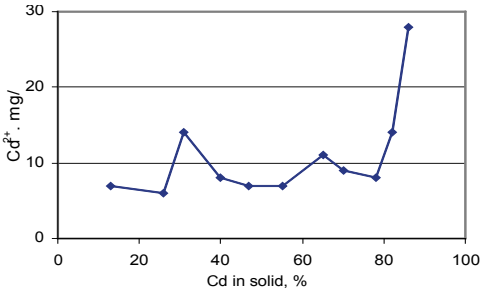


Fig. 32. Cd concentration in outcoming solution as function of the Cd concentration in the bed material.

The constant Cd^{2+} level reveals that the precipitation rate was independent of the crust thickness until the Cd content in the precipitate had increased to about 80%. The decrease in the rate after this point was most probably caused by complete consumption of the smallest Zn particles and not by the thickening layer of Cd. Cd has thus mostly precipitated onto the outer Cd surface and the Zn corroded from beneath the Cd layer. The Zn ions again had been diffusing through the layer. This indicates that diffusion of Cd^{2+} and Zn^{2+} ions through the product layer could not have been a limiting factor.
Thus the reduction, the cathode reaction

$$Cd^{2+} + 2e^- = Cd \tag{50}$$

is mostly taking place on the outer surface, whereas the anodic oxidation on the Zn surface inside:

$$Zn = Zn^{2+} + 2e^- \tag{51}$$

and the electron current is conveyed through the Cd layer.

Apart from achieving a high grade Cd precipitate and a good utilization of the Zn powder, the mechanically very stable Cd layer and very small quantities of finely divided loose dendrites was interesting. If such a precipitate could constantly be produced in the plant it could be possible to replace the filtration of the solution after the precipitation with thickeners or hydrocyclones, which would be less expensive and need less labor.

To avoid excess dendrite formation in electro-winning of metals, the primary means is to restrict the current density. In the case of Cd, which is especially susceptible to dendrite formation, the electro-deposition is normally performed at 50 to 100 A/m^2 compared to 300 to 600 A/m^2 for Zn. A low temperature also restricts dendrite formation. As cementation is a type of electro-deposition, it was presumed that the same factors could possibly be of importance in this case, too. In the above cementation experiments, the radius of the Zn powder particles were about 0.12 mm and the time for complete consumption about 24 h. This gives a corrosion rate of about 0.005 mm/h, corresponding to an exchange current density of around 2.5 A/m^2.

The precipitation rate can most probably be written as:

$$dC_{Cd2+}/dt = k*A_{Zn}*C_{Cd2+} \tag{52}$$

where A_{Zn} is the initial surface area of the Zn powder. As the surface area of the powder is directly proportional to the amount of Zn powder, A_{Zn} can be substituted by the mass of Zn, m_{Zn}, and k will then be specific for the type of Zn powder used. The “Zn powder specific” precipitation rate is then:

$$(dCd/dt)/m_{Zn} = k*C_{Cd2+} \quad (53)$$

To keep the precipitation rate low, $k*C_{Cd2+}$, should be kept low. As the rate, and accordingly k, will increase with temperature (**IX**), low temperature would be advantageous. Technically it would be possible to cool the solution down to around 40 °C without crystallizing out sulfates. The temperature of the incoming solution is, however, determined by the conditions in the preceding Co removal step, which was operated at about 85 to 90 °C. Due to the cooling arrangement in the plant, cooling of this solution would require the construction of a new cooling step. For economical reasons, therefore, the temperature should preferably be kept at its "natural" level, about 70 - 75 °C, and all experiments for dimensioning were made at this temperatures.

A number of small-scale experiments, like the one referred to above, confirmed that a concentration of 10 mg/l Cd^{2+} in the bed should be sufficiently low to give a smooth-surfaced deposit. To achieve this concentration already in the first reactor, a bed with a sufficient quantity of Zn powder would be needed. With ideal mixing of the system the mass balance becomes:

$$\overset{*}{V}\,(C_0 - C)_{Cd2+} = k*m_{Zn}*C_{Cd2+} \quad (54)$$

where $\overset{*}{V}$ is the volumetric flow rate of the feed solution, $(C_0 - C)_{Cd2+}$ quantity precipitated cadmium, m_{Zn} amount of Zn powder present and C_{Cd2+} cadmium concentration in the bed solution, which in an ideally mixed bed is the same as the concentration of the final solution. The system is thus independent of the reactor volume, which than can be chosen freely from an engineering point of view.

Due to its simplicity, the first choice for technology was a straight forward fluidized bed system, which implied that the Zn powder had to be sufficiently coarse to be retained in the bed. Studies on this showed that a sufficient quantity of a suitable fraction of Zn powder could be obtained from the plants normal Zn powder production. The rate constant, k, at 75 °C was for this fraction experimentally found to be about 2.2 $m^3h^{-1}kgZn^{-1}$.

With C_{0Cd2+} and C_{Cd2+} respectively 300 and 10 mg/l, m_{Zn} in the first bed would be about 13 kg per m^3/h of flow through the bed. In a plant, with a capacity of 200000 ton of Zn/a, the solution flow is about 250 m^3/h, which means approximately 4 t of Zn powder would be needed in the first bed. On this basis development of a suitable reactor was undertaken [**VI**].

It became soon clear that, even with 10 mg/l of Cd^{2+} in the out-coming solution from the first bed, a system based solely on fluidization by the upward flow of solution was still very sensitive to agglomeration. To reduce eventual Cd^{2+} concentration gradients, mechanical agitation was added to increase the mixing of the bed. The final solution adopted, was a reactor where the main fluidization was conducted by the upward flow of the solution. An agitator was placed at the bottom and a conical settling part above the bed. A sketch of the reactor is shown in Fig. 41.

Even this reactor, however, was susceptible to agglomeration. Due to the similarity of the cementation reaction to electrowinning of metals where leveling agents are added to obtain a more even current distribution, addition of an organic polymer as a leveling agent was tested. The results were very positive and prolonged testing did not reveal any tendencies of agglomeration. A full scale reactor was constructed and tested with likewise good results and decision of adopting the process in the plant was made.

A typical Cd^{2+} content, i. e. 200 to 400 mg/l, in the plant feed solution and 10 mg/l in the outgoing means a reduction factor of 20 to 40 for Cd^{2+}. Thus 3 identical reactors in series would give an end solution of less than 0.1 mg/l of Cd^{2+}. To guarantee the operational reliability even at longer down-times of a reactor, a system with 5 reactors was chosen for this first generation system. The solution flow through the reactor series was conducted by maintaining a hydrostatic head though the series.

With the long residence time for the solid phase in each reactor, about 24 h, a simulated moving bed operation mode seemed very convenient. When the Cd concentration in the bed of the first reactor reached the desired level, 80 to 90% of Cd, the reactor was de-connected and emptied, than re-batched with Zn powder and re-connected as the last one in the series. The principle of the operation is shown in Sequences 1 and 2 in Fig.33.

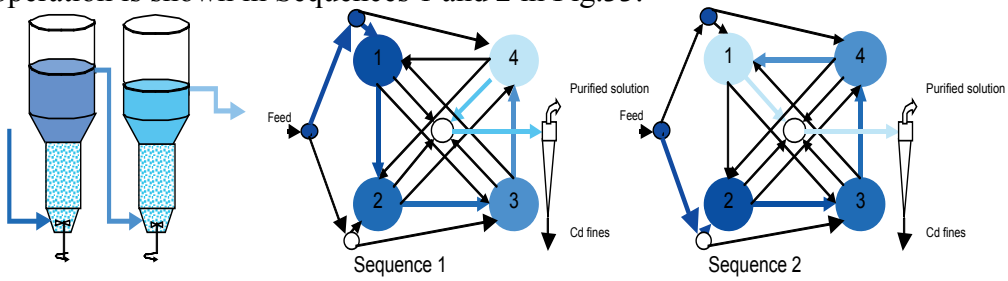


Fig. 33. Outline of the Cd reactors and the principle of the practical operation.

This system for Cd removal has been in operation since 1974, and it is the only system used industrially which applies the principle presented here. It is even, as far as known, the only one using a dense bed principle, as no industrial application of other developments has been found reported.

4 PROCESSES FOR LEACHING OF CONCENTRATE [X, XI]

4.1. Introduction

In the 1980´s the productivity of the plant was falling behind the main competitors, which had, or were, increasing capacities of their plants substantially. At that time, the market for sulfuric acid was deteriorating, and preliminary calculations showed that an expansion of the plant on the basis of the roast-leach process was not very attractive.

At some plants, which earlier had faced problems with marketing of sulfuric acid, expansions had been undertaken by employing direct leaching of concentrate. A process based on leaching in autoclaves at 150 °C had been put into operation in 1981 by Cominco at Trail, Canada [39, 40]. In this process, sulfur was obtained in elemental form, and the leaching was normally presented to take place according to the following reaction:

$$2ZnS + O_2 + 2H_2SO_4 => 2ZnSO_4 + 2H_2O + 2S \quad (55)$$

Even though the autoclave technology could be regarded as rather reliable, it was considerably more demanding than the normal technology used in zinc plants, where only non-pressurized reactors were operated at temperatures below 100 ℃. Also, the investment and maintenance costs for the autoclaves were high.

Investigations on leaching of sulfide concentrates at temperatures below 100 °C had been done, - mostly in chloride media, but also some work on sulfate-based systems had been published [41-44]. It had been established that oxidation directly by oxygen according to reaction (55), is very slow and become hindered by passivation of the sulfide surface, but oxidation by ions like NO_3^-, Cu^{2+} and Fe^{3+} gave much higher rates and no severe passivation. The active reagents could be regenerated by oxidation with oxygen gas or air. In the case of leaching a Zn concentrate, the natural choice of leaching medium would be ferric ions, Fe^{3+}, as the concentrate itself would provide the iron. The leaching and regeneration reactions would then be

$$ZnS + Fe_2(SO_4)_3 => ZnSO_4 + 2FeSO_4 + S \quad (56)$$

$$2FeSO_4 + H_2SO_4 + 0.5O_2 => Fe_2(SO_4)_3 + H_2O \quad (57)$$

Other sulfides such as FeS, CuS, CdS, and PbS in the concentrate, either in the sphalerite lattice or separate, react similarly to ZnS:

$$MeS + Fe_2(SO_4)_3 => 2FeSO_4 + MeSO_4 + S \quad (58)$$

The influence of temperature, ferric and ferrous iron concentrations, composition of the sphalerite and especially the iron content in the sphalerite lattice on the reaction rate had been studied. The determined activation energies varied between 40 and 90 kJ/mol, and the reaction order with respect to ferric iron concentration had be found to vary between 1/3 and 2/3. The leaching rate had been found to increase about linearly with the iron content in the sphalerite lattice.

A single kinetic model that would describe the leaching behavior up to the over 98 - 99% extraction region, which would be the aim in an industrial application, had, however, not been demonstrated. A mixed model assuming clean surface and chemical control up to about 60% extraction, followed by diffusion control onwards was proposed by Bobeck and Su [41]. Their experiments were performed on a -100 +150 mesh fraction, or a particle size of about 100 to 150 µm. Even though studies on extractions approaching 100% were not found in the literature, results presented by Bobeck and Sun indicated though, that to achieve such extractions from the mentioned grain size fraction, a leaching time of 20 to 30 h at 95 °C could be needed.

Due to the apparent simplicity and the low cost of non-pressurized reactors, work to investigate the possibilities to develop an industrial process based on leaching at atmospheric pressure was commenced.

4.2 Development work on concentrate leach processes

4.2.1 Process for leaching of bulk concentrate

Appreciable quantities of the global zinc resources were found in the so-called complex ores, which mostly consists of a mix of finely dispersed ZnS and PbS grains. Due to the fineness, separation of the ore into separate Zn and Pb concentrates was not done, but a bulk concentrate was produced. This was treated in pyrometallurgical processes. Besides high contents of Pb, these concentrates normally had high contents of Ag, and all three elements were recovered with high efficiency in these processes. The feed to the roaster in the existing plant at Kokkola consisted of “clean” Zn concentrates; meaning less than about 2% Pb and low SiO_2 and Cu contents to avoid agglomeration of the bed material by low-melting phases. Agglomeration could be avoided by lowering the temperature of the bed, but then the capacity of the roaster would decrease. In a direct leach operation, such “dirty” concentrates would not cause

any significant physical or mechanical problems, and it would give more flexibility in purchasing of concentrates.

In the leaching, zinc would be recovered to the solution and a similar Pb/Ag residue as in strong acid leaching of ferrite would be obtained after removal of the elemental sulfur. This residue had very low, if any, commercial value, unless it was high-grade with respect to both Pb and especially Ag. The problem with $PbSO_4$ residues, though, had at this time already been addressed within the company, and a process had been developed by Rastas and co-workers, where Pb and Ag were converted to sulfides and recovered by flotation into a high-grade sulfide concentrate at high recovery rates [45]. Thus bulk concentrates could be a major feed source for the plant in the future. Consequently, a study was initiated to investigate the possibility to integrate an atmospheric leaching of bulk concentrates into the existing process.

Apart from precipitating as $PbSO_4$, Pb can also form plumbojarosite, $Pb[Fe_3(SO_4)_2(OH)_6]_2$:

$$3Fe_2(SO_4)_3 + PbS + 0.5O_2 + 11H_2O \Rightarrow Pb[Fe_3(SO_4)_2(OH)_6)]_2 + 5H_2SO_4 + S \quad (59)$$

The Pb in this compound could not be sulfidized directly, but it had first to be decomposed, and, with 6 mol of Fe per mol of Pb, even moderate quantities of this jarosite could easily make the Pb/Ag residue valueless. Equation (59) indicates that high $Fe^{3+}$and low H_2SO_4 concentrations should promote the jarosite precipitation, and thus the balance between these two would be an important parameter to control in the leaching of bulk concentrates. Dutrizac had studied formation of plumbojarosite and showed that it is less stable at 97 °C than at 150 °C, i. e. at the temperature used in the autoclave leaching [44]. This was in favor of an atmospheric process, however, the conditions needed to avoid precipitation under industrial conditions were not known.

When leaching bulk concentrates combined with Pb/Ag recovery, simultaneous recovery of Pb and Ag in the calcine of the existing process could also become feasible. Then, both in the ferrite and the concentrate leaching steps, the iron had to be brought into solution, leaving Pb/Ag as a low-iron $PbSO_4$ residue. The question still was how to combine the leaching of the two materials in the most beneficial manner. In such a process, ferrite leaching

$$ZnOFe_2O_3 + 4H_2SO_4 \Rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad (60)$$

is favored by high acid concentration, whereas leaching of the concentrate according to reaction (61) should be independent of acid concentration, but favored by high Fe^{3+} concentration:

$$ZnS + Fe_2(SO_4)_3 => ZnSO_4 + 2FeSO_4 + 2S \quad (61)$$

The ferrite would provide for high levels of iron in the solution, which would give a rapid leaching of the concentrate. It should then be advantageous to separate the two reactions to leach ferrite at the front of the leaching and the concentrate at the end. The iron primarily leached from the ferrite, reaction (60), would, however, provide for only a fraction of the quantity needed to leach a sufficient amount of Zn to make an expansion of the plant profitable. The rest of the needed ferric iron would then be regenerated by oxidation, resulting in the overall reaction (62):

$$ZnS + (2FeSO_4) + H_2SO_4 + 0.5O_2 => ZnSO_4 + (2FeSO_4) + 2S + H_2O \quad (62)$$

If all acid needed in the leaching of the concentrate was added to the ferrite leach step, the acid concentration would increase considerably, and thus increase the reaction rate of the ferrite. Then it should be advantageous to start oxidation first when the major part of the ferrite has been dissolved, like shown in the flowsheet shown in Fig. 34.

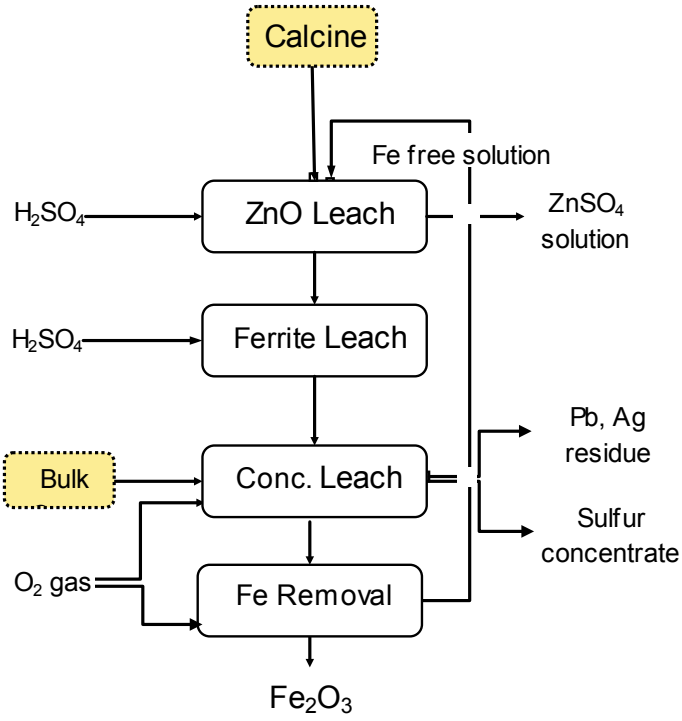


Fig. 34. Flowsheet for combined treatment of concentrate and ferrite for maximum recovery of Pb/Ag.

To recover all Pb/Ag in the calcine, the iron precipitation should then, to avoid losses with the iron residue, be performed without neutralization. For this purpose, the only available technology at that time was hematite precipitation in autoclave, which Dova Mining, Japan and Ruhr Zink, Datteln, Germany were operating. Then the solution would be NH_4^+-free and difficulties with NH_4^+-jarosite formation acting as seed for Pb- jarosite in the leaching steps could be avoided or at least strongly suppressed.

Even though the experiments on this technology showed very promising results, the development of the process was terminated, and it was not implemented in the Kokkola plant. Mostly this was because of a pyro-metallurgical process for the production of Zn directly from concentrates under development within the company by Talonen *et al.*[47]. This process looked very promising also for treatment of bulk concentrates Development in ore beneficiation had also led to improvement in production of separate Zn and Pb concentrates, and available quantities of bulk concentrates was hence foreseen to be decreasing considerably. The expansion of the plant had then to be based on a feed of normal Zn concentrates.

A process suitable for treatment of bulk concentrates, with a flowsheet mainly as shown in Fig. 42 was, however, patented, and have been licensed and implemented industrially elsewhere [**X**].

4.2.2 Process for leaching of Zn concentrate

With the leaching based on normal Zn concentrates, the feed to the leaching would also in the future continue to contain low levels of Pb/Ag. Consequently, the non-existing economical incentive in recovering these metals would greatly remain unchanged. No gain could then be achieved by producing a high grade Pb/Ag residue, and, accordingly, iron could be precipitated during the leaching like in the existing conversion process for ferrite and the autoclave processes for concentrate leaching. For simultaneous precipitation of iron at a temperature below the boiling point of the solution only precipitation of jarosite would come into question, as hematite precipitation needs higher temperature, and goethite precipitation needed so high pH that the concentration of Fe^{3+} would be too low to give an acceptable leaching rate for the concentrate. Development work was then focused on clarifying weather a leaching process of Zn concentrates with simultaneous precipitation of jarosite could be commercially viable. Fig. 35 shows the conceptual process flowsheet for this approach.

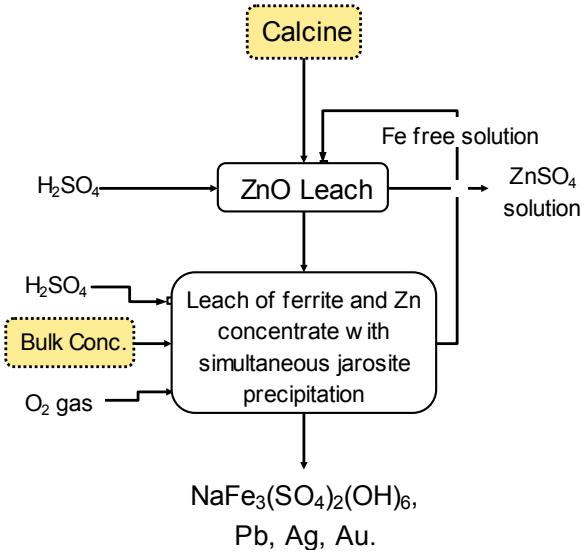


Fig. 35. Conceptual flowsheet of combined leaching of ferrite and Zn concentrate with jarosite precipitation.

Important parameters to control and issues to develop would then be:

- influence of Fe^{3+} and H_2SO_4 concentrations on the leaching.
- choice of concentrate for the direct leaching out of the 15 to 20 different ones fed to the plant.

Demands on the reactors:

- with the long reaction time needed they should be large and have a low energy demand for mixing
- effective oxidation of ferrous to ferric iron with high utilization of the oxygen
- should be able to handle the S/MeS froth formation that would form in the reactor, and could stay on the top.

4.3 Experimental

Influence of H_2SO_4 and temperature on the leaching rate was investigated in batch experiments in laboratory scale. These experiments were performed on a bulk concentrate which contained respectively 33.9, 16.6 and 8.3% of Zn, Pb and Fe. The leach solution contained initially 10 g/l Fe^{3+}. The quantity of the concentrate was chosen to leave about 3 g/l Fe^{3+} in solution at 100% extraction of the sulfides. H_2SO_4 concentrations of 10, 25, 50 and 100 g/l, and temperatures of 40, 60, 80 and 95 °C were examined.

The influence of Fe^{3+} concentration was studied in batch experiments with initial concentrations of 10, 5 and 2 g/l Fe^{3+} and 10 g/l H_2SO_4 at 95 °C. These experiments were performed with a conventional Zn concentrate with concentrations of Zn, Pb, and Fe respective 52.5, 0.4 and 10.1%. The amount of concentrate added was equivalent to a consumption of about 1.4 g/l Fe^{3+} at 100% Zn and Fe extraction. As the initial leach solutions in all these experiments did not contain any Zn^{2+}, the leaching rate was determined from Zn^{2+} in solution, and the final extraction from the leach residue.

4.3.1 Results and modeling

The experimentally obtained data as well as the fit of the Avrami model are displayed in the diagrams in Figs. 36 - 42.

The model for the influence of temperature was calculated by optimizing *k* and *n* for the four experiments individually, (individual *n* each experiment) and with *n* constant in all four experiments. R^2 with individual *n* was 0.990 and with constant 0.977. In Fig. 36 is revealed the experimentally obtained data and the fit of the model with constant *n*. The obtained average value for constant *n,* = 0.518, whereas the average for the four variable *n* was 0.533.

The temperature dependence for *k,* with *n* = 0.515, at all temperatures gave a trendline equation as shown in Fig. 37. The so obtained equation for the trend line was used to calculate the needed reaction times, *t*, to reach equal extraction (50 %) at the different temperatures. The activation energy, E_a, was then calculated from the Arrhenius plot where $k = 1/t$ (Fig. 41).

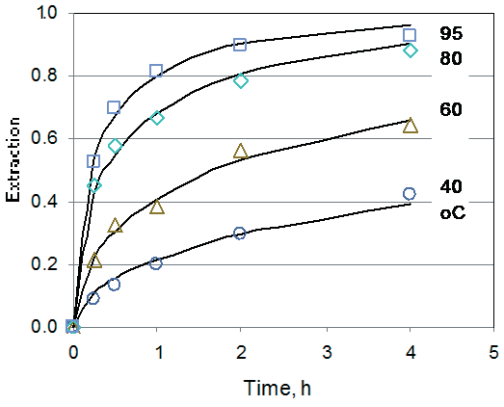


Fig. 36

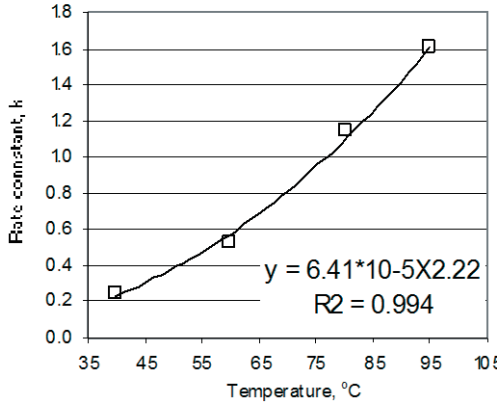


Fig. 37

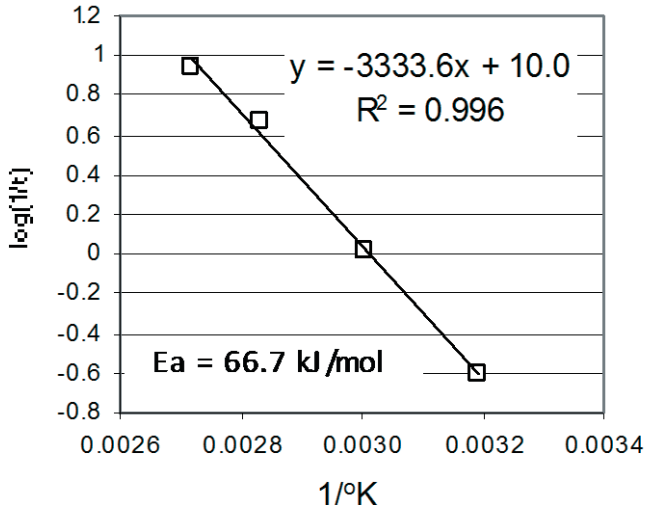


Fig. 38

Fig. 36 - 38. Leaching of bulk concentrate at different temperatures with calculation of *Ea.*

Using the Celsius temperature scale in the Avrami model, the following equation was obtained for the progress of the leaching:

$$X = 1\text{-}\exp(-6.41*10^{-5}*(t/°C)^{2.22}*(t/h)^{0.515}) \qquad (63)$$

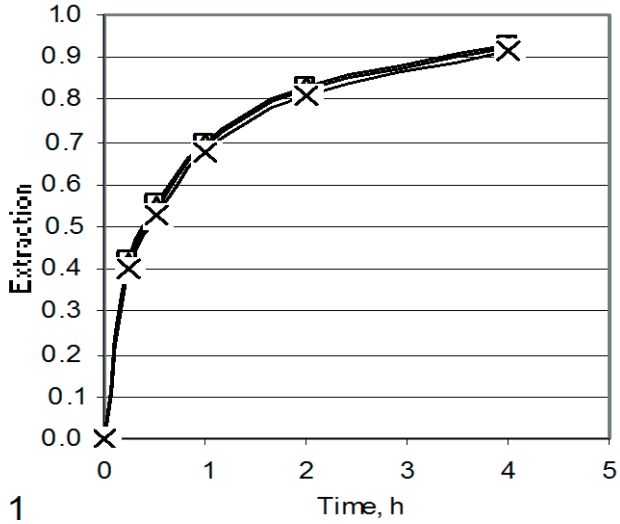


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Fig. 39. Leaching of bulk concentrate at 10, 25, 50 and 100 g/l H_2SO_4. Initially 10 g/l of Fe^{3+}.

Fig. 39 reveals the results of the experiments on the influence of H_2SO_4 concentration on the leaching. All four trendlines for the tested acid concentrations coincide, showing that at least down to 10 g/l of H_2SO_4 no detectable influence on the leaching rate is found. This independency has also been reported in the literature [45 - 47].

Then the leaching rate will only be dependent on the concentration of Fe^{3+}, and assuming that the reaction rate would be exponentially dependent on the Fe^{3+}, the Avrami model for the extraction becomes simply:

$$X = 1-\exp(-k*Fe^{nFe}*t^{n}) \quad (64)$$

Even though the leaching rate in these experiments is independent of the acid concentration, this will not be the case in plant operation. In a plant with jarosite precipitation the solution will contain NH_4^+ ions, which together with the acid concentration will influence the Fe^{3+} content in the solution. From Fig. 8a (section 2.2.2.) is seen that at 10 g/l H_2SO_4 and 1 g/l NH_4^+ the Fe^{3+} concentration will in equilibrium with jarosite be about 1 g/l, which will be very low to be of interest in an industrial leach operation, accordingly, an acid concentration much lower than about 20 g/l of H_2SO_4 will hardly come into question.

The influence of Fe^{3+} is revealed in Fig. 40, 41 and 42. The Avrami model gave by optimizing of the individual experiments (determination only of *k* and *n*) gave the a fit ($R^2 = 0.993$) that is visualized in Fig 40. Fig. 41 shows the fit of model equation (64) to a combined optimization of the three leach experiments. The obtained Avrami model equation became as shown in equation (65). The obtained degree of explanation was 0.987, or slightly below the figure obtained in the optimization of the individual experiments, but is still very god.

$$X = 1-\mathrm{Exp}(-0.3068*Fe^{0.4367}*t^{0.8292}) \quad (65)$$

The reaction time, *t*, needed to reach the same extractions at the three different Fe^{3+} concentrations was calculated with this model equation, (65). The *1/t* - Fe^{3+} plot (Fig. 42), show the reaction rate being proportional to $[Fe^{3+}]^{0.53}$, or, close to the square root of the Fe^{3+} concentration. Both this reaction order of 0.53, the independence of H_2SO_4 concentration and the above found activation energy, 66.7 kJ/mol, are all well inside the figures reported in the literature [46, 47].

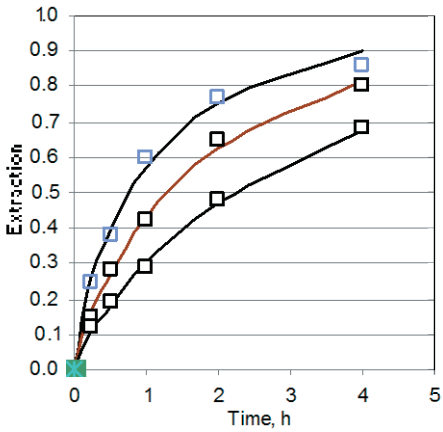

Fig. 40

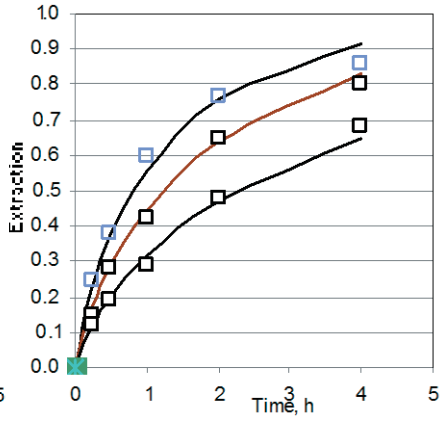

Fig: 41

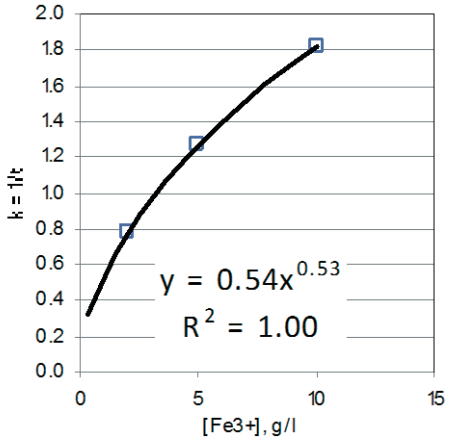

Fig. 42

Fig. 40 – 42 .Influence of Fe^{3+}on leaching of Zn concentrate at 95 °C. Fe^{3+}= 10, 5, 2 g/l. Separate modelling of the experiments with Avrami in Fig. 44, and combined in Fig. 45. The reaction order for ferric iron is given in Fig. 46.

4.3.1.1 Laboratory experiments on the process for bulk concentrates.

Bulk concentrate, 100 g/l, with Zn, Pb and Fe concentrations of respective 33.9, 16.6 and 8.3 wt%, together with 66 g/l ferrite residue containing Zn, Pb and Fe 23.5, 6.0 and 33.5 wt% were added to an NH_4^+-free solution containing 50 and 171 g/l, respectively of Zn and H_2SO_4. The temperature was 95 °C and 2 bar O_2 gas pressure was applied after two hours and continued up to eight hours of total leaching time. The experiments were performed in an autoclave

to control the oxygen pressure. The progress of the experiment is shown in Table 7.

Table 8. Leaching of a mix of a bulk concentrate and ferrite residue.

Time, h		Solution, g/l			Solid,%			Extraction,%	
		Fe_{tot}	Fe^{3+}	H_2SO_4	Zn	Fe	Pb	Zn	Fe
0		0	0	171	29.8	18.3	12.5		
1		21.5	0	69.4					
2	O_2 on	21.5	0	67.3					
3		19.7	6.2	40.9	12.9	7.2	24.9	79.1	81.1
5		20.8	13.5	26	4.3	6.9	25.4	93.2	82.3
8		21.6	17.3	24.5	0.8	3.4	32.8	98.8	93.2

Most of the ferrite is leached during the first hour. All the dissolved ferric iron has also reacted further with the concentrate. Leaching of the rest of the concentrate is much slower, even with a rather high concentration of Fe^{3+} during the rest of the experiment. Extraction of Zn calculated on the total Zn added was 98.8%.

From such Pb/Ag residues, a PbS concentrate with about 65 - 70 % Pb could be produced by the sulfidation/floatation process developed by Rastas *et al.*[45].

Traces of Pb-jarosite were, however, detected by XRD in the final residue. This shows that with longer retention times, jarosite will form even in solutions devoid of the jarosite forming ions NH_4^+ and Na^+. In plant operation, where recycling of jarosite in the process can "infect" the whole circuit, the problem with Pb-jarosite in the leach residue could become more serious than what the results of this experiment indicate. A possibility to reduce jarosite formation could be to reduce the Fe^{3+} concentration during the leaching stage by controlled oxidation which would mean longer leaching time.

As the project with bulk concentrate was terminated, the problem with jarosite formation was not studied further.

4.3.1.2 Laboratory experiments on the process for Zn concentrates.

The leaching rate of the most abundant concentrates fed to the plant was investigated by leaching in a solution containing 10 g/l each of $Fe^{3+}$and H_2SO_4 at 95 °C. The quantity of concentrate added, about 7 g/l, was chosen to leave about 3 g/l of Fe^{3+} in the solution at 100% extraction of Zn from the sulfides.

Fig. 43 illustrates the even a five-fold differences in leaching rate was found between the concentrates. As the supply of the fastest leaching concentrates

was too limited to base the plant expansion on, the dimensioning work was performed on a concentrate with the most reliable long-term supply. This concentrate had, however, a rather low specific leaching rate.

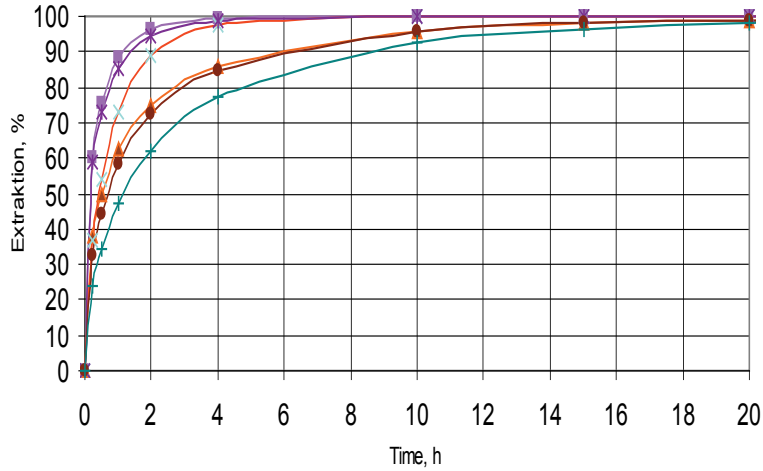

Fig. 43 Fit of the Avrami model to the leach results from 6 different concentrate.

The Avrami model was applied to the results of these experiments, and found to fit well to all concentrates with a degree of explanation (R^2) ranging from 0.960 to 0.992. The values for *k* and *n* varied between 0.64 and 2.1 respectively 0.51 and 0.75.

4.4.1.4 Pilot runs

The questions that had to be resolved in a commercial leaching operation had become familiar during the laboratory works, and had also been met in earlier projects. These issues included:

- handling of the elemental sulfur/sulfide froth that would collect on the top of the reactor.

- slow re-oxidation of Fe^{2+} to Fe^{3+} by oxygen at temperatures near the boiling point of the solution.

- attaining a high O_2 gas efficiency.

- minimizing the energy consumption for mixing.

To deal with these issues a reactor equipped with a central draft-tube and a double action, pumping/mixing, impeller below the tube was chosen. The impeller brought about dispersion of the oxygen gas as well as the mixing to

hinder settling of the coarse material by generating a circulating flow up on the outside and down within the tube The down-flow should carry down and re-circulate both the sulfur/sulfide froth and "escaped" oxygen in the gas volume on the top of the reactor, and mix all back into the bulk slurry. Fresh oxygen was injected below the impeller. The height of the reactor provided a hydrostatic pressure of about 2.5 bar to ensure a reasonable partial pressure of oxygen in the gas bubbles even at a temperature close to the boiling point of the solution. The development of the mixing and oxygen dispersion was followed through the concentrations of Fe^{3+} and Cu^{2+} in the solution. To ensure the presence of Fe^{3+} ions in the solution from the start of the experiments Cu^{2+} should be on an acceptable level also in this phase.

The experiments necessary for the dimensioning of the reactor and optimizing the leaching conditions were performed by Takala *et al*. according to the flowsheet displayed in Fig. 35 [48]. All feed streams were taken from the operating plant.

The main parameters regarding the leaching rate were the acid and ferric iron concentrations in the solution and the leaching rate of the different concentrates.

Preliminary energy balance calculations showed that, when using O_2 gas, the process would be autogenous with respect to the heat requirement to increase the temperature to the boiling point of the solution. Thus the influence of the temperature was not investigated in the pilot experiments, but it was kept close to the boiling point of the solution in all experiments.

The reactor was filled with slurry from the conversion process in the plant and feeding of O_2 gas was started, where after 67 g/l of Zn concentrate with 52% Zn, 32% S and 4.5% of Fe was added. The leaching time was 28 h. Analyses from a typical experiment are presented in (**XI**).

4.3.1.5 Discussion of the results from pilot runs on concentrate leaching

The behavior of acid, ferrous and ferric iron is displayed in diagram 1 in Fig 49. Extraction of Zn obtained from the "Example" in paper **XI** and the result of a standard leach in laboratory on the same concentrate are shown in diagrams 2 and 3.

The Avrami model was fitted to both experiments with good fit for the laboratory experiment, whereas in the pilot experiment, the fit above 90% extraction is poorer, as seen also in Table 9. It seems as an unexpected increase in rate in the period between 12 and 20 hours. This effect has been noticed in a number of similar pilot experiments.

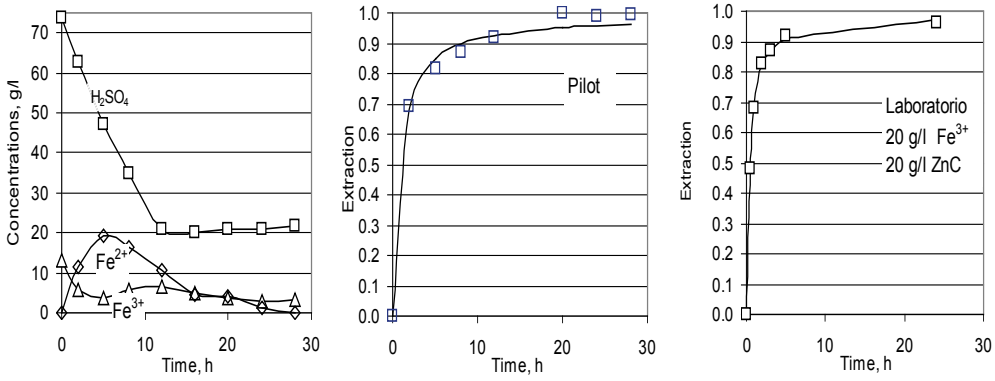

Diagram 1 Diagram 2 Diagram 3

Fig.44: Behavior of the acid and iron, diagram 1, and extraction, diagrams 2 and 3, during a batch pilot run on concentrate leaching. The lines in diagrams 2 and 3 are obtained with the Avrami model. Extraction in the pilot run is calculated on Zn in the concentrate and solid samples during the run.

Table 9. Fit of the Avrami model to the laboratory and pilot experiments in Fig. 44.

Avrami model	k	n	R^2
Laboratory	1.18	-0.767	0.997
Pilot	0.58	-0.810	0.863

Diagram 1 reveals that following reactions are the main ones during the first hours

$$Fe_2(SO_4)_3 + ZnS = ZnSO_4 + 2FeSO_4 + 2S \quad (66)$$

$$2FeSO_4 + 0.5O_2 + H_2SO_4 + ZnS = ZnSO_4 + 2FeSO_4 + S + H_2O \quad (67)$$

$$2NaFe_3(SO_4)_2(OH)_6 + 6H_2SO_4 + 3ZnS = 3ZnSO_4 + 6FeSO_4 + Na_2SO_4 + 12H_2O + 3S \quad (68)$$

whereas reaction (69)

$$6FeSO_4 + Na_2SO_4 + 3O_2(g) + 3ZnS + 6H_2O = 2NaFe_3(SO_4)_2(OH)_6 + 3ZnSO_4 + 3S \quad (69)$$

starts after about five hours. The calculations for the over-all balance for the experiment are seen from Table 10. The solid content of the conversion slurry was not determined, but it was calculated by assuming that all sulfur in the concentrate, which is known, has been converted to elemental sulfur in the final residue. The iron balance is calculated from analyses marked yellow, quantity of solid material is obtained from the iron balance, and finally the Zn

balance from the Zn content in solid. The point at 16 h has been left out because of a clearly deviating value for Zn in the solid at this point.

Table 10. Elementary balance for the leach experiment in Fig. 49-1. The yellow marked figures are based on analyses and measured quantities.

	S	Fe	Zn
IN		g/l	
1 Conc	21.3	3.0	34.6
2 Solution		13.4	
3 Conv. Solid		9.1	1.1
Total In	**21.3**	**25.5**	**35.7**
OUT			
4 Final residue	21.3	22.3	1.4
5 Final solution		3.2	34.3
Total Out	**21.3**	**25.5**	**35.7**

The leaching did practically proceed to completion within 20 hours. The end-concentrations of H_2SO_4 and Fe^{3+} (in Fig.44 diagram 1) correspond are very close to the equilibrium concentrations obtained in the experiments on solubility of jarosite at 2 to 3 g/l of NH_4^+ shown above (section 2.2.2, Diagram 8). This implies that with the time needed to reach the sufficient extraction of zinc also the ferric iron in solution is very close to its equilibrium.

The main parameters regarding the leaching rate would be the temperature, ferric iron concentration in the solution and the specific leaching rate of the concentrate(s). Preliminary energy balance calculations showed that, when using O_2 gas, the process would be autogenous with respect to heat requirement to increase the temperature to the boiling point of the solution. Hence all leaching experiments were made at temperatures close to this point.

With jarosite present, the H_2SO_4 and NH_4^+ concentrations would determine the minimum (= equilibrium) Fe^{3+} concentration, which, with the long reaction times needed, would be approached at the end of the leaching. The optimal concentration levels of H_2SO_4 and NH_4^+ were contradictory; - the acid increases the Fe^{3+} concentration but also the volume flow, whereas NH_4^+ advances the jarosite precipitation, but lowers the Fe^{3+} content in the solution.

5 PROCESS BASED ON HYDROLYTIC PRECIPITATION OF JAROSITE [XII]

5.1 Introduction

The requirement to use neutralizing calcine in the iron precipitation is, both in the Jarosite and Goethite processes, an obstacle for reaching a maximum recovery of all valuable elements in the concentrates. Pb/Ag/Au, being insoluble, stay in the iron residue, and In, Ga and Ge, which have been leached in the high acid leach, will be re-precipitated with iron. For a custom smelter, which is treating a number of different concentrates, the choice of concentrates will then be limited, or costly, when otherwise suitable concentrate has to be rejected due to payable contents of these unrecovered elements.

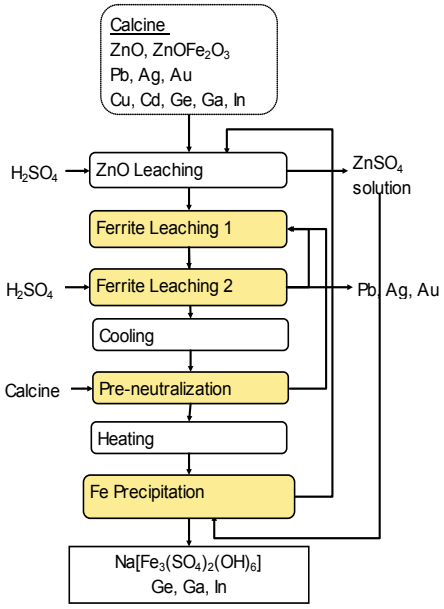

Fig. 45. The Low-contaminant Jarosite Process.

To recover all these elements, the process should produce a high grade leach residue from which Ag, Pb, and Au can easily be extracted, and In, Ga, and Ge should be obtained in a solution with iron in the ferrous state. From such a solution, these elements can be precipitated by simple neutralizing of the solution. Dowa Mining's autoclave process has all these options, but high costs for a revamping of a jarosite process on the basis of Dowa's technology would certainly not be paid for by the recovery of only the mentioned metals, at least not at the time when the decisions on adopting the Conversion Process were made at Kokkola.

As seen above, the basis for the development of the Conversion Process was the finding that jarosite will precipitate at rather high acid concentrations, even up to above 30 to 40 g/l of H_2SO_4:

$$3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 12H_2O \Rightarrow 2NH_4[Fe_3(SO_4)_2(OH)_6] + 6H_2SO_4 \qquad (70)$$

This was also utilized by Electrolytic Zinc of Australasia, EZA, in the development of a process, "The Low-contaminant Jarosite Process", which is illustrated in Fig. 45. In this process, iron was hydrolytically precipitated, as

jarosite without neutralizing (reaction 70). They were then able to recover all Pb and Ag in the calcine into one high acid leach residue with a simultaneously increased recovery of Zn, Cu and Cd.

To precipitate a sufficiently large portion of iron in this process, the final acid concentration had to be maintained so low that a thorough pre-neutralization of the feed solution from the ferrite leach was necessary. This solution was coming from the leaching at a temperature of about 100 °C, and, as it will always contain residual NH_4^+ or Na^+ ions, precipitation of jarosite during pre-neutralization at such a high temperature could not be prevented. Therefore, to evade this problem, it was found necessary to lower the temperature of the ferrite leach solution to about 50 °C before this step. This again implied re-heating of the solution before the jarosite precipitation step. To save energy, counter-current heating with hot plant solutions was employed and scaling in the heat exchangers was a major problem. Even with these measures it was found necessary to dilute the pre-neutralized feed solution with neutral solution to keep the final acid concentration low enough to obtain the sufficient degree of iron precipitation. This process would give very high extractions of both Zn and all other soluble non-ferrous metals, and a Pb/Ag/Au residue that would contain all of these metals coming in with the calcine. With iron in the ferric state In, Ga, Ge would, however, be re-precipitated and lost with the jarosite. The difficulties in the process added, however, so much cost both for the investment and heating, which together with the mechanical problems, led to the decision that the process as such was not realized industrially [53 - 57].

5.2 New process for combined calcine and concentrate leaching

5.2.1 Introduction

The described difficulties with the EZA process, both during pre-neutralization and jarosite precipitation, was brought about by iron being in the ferric state. If, on the contrary, the iron would be in the ferrous state, the pre-neutralization could be done without cooling, and, as ferrous iron hydroxide is more soluble than zinc hydroxide, the solution can be completely neutralized also at high temperatures without any risk for iron precipitation.

The problem would then be to precipitate iron without neutralization from the ferrous iron solution. Known technologies were hematite precipitation at 180 - 200 °C and hydrolytic precipitation of jarosite at 150 -190 °C and elevated oxygen pressure as demonstrated by Sefton [57].

On the basis of own experience, it was assume thought idea that there could be a possibility to precipitate a sufficient degree of iron also at temperatures below the boiling point of the solution. The reaction equation for hydrolytic jarosite precipitation through oxidation of ferrous iron,

$$6FeSO_4 + (NH_4)_2SO_4 + 1.5O_2 + 9H_2O \Rightarrow 2NH_4[Fe_3(SO_4)_2(OH)_6] + 3H_2SO_4 \quad (71)$$

shows that compared to precipitation from ferric iron solutions, (reaction 70) only half the amount of acid is liberated per unit of iron. By adding the ammonium ion as ammonia into the precipitation, even less acid would be formed:

$$6FeSO_4 + 2NH_3 + 1.5O_2 + 9H_2O \Rightarrow 2NH_4[Fe_3(SO_4)_2(OH)_6] + 2H_2SO_4 \quad (72)$$

In a typical zinc plant, the maximum iron concentration that can be reached in the leach solution is around 25 g/l, which implies that the need for precipitation would thus be around 20 g/l of iron. According to reactions (71) and (72), this would liberate 18 respective 12 g/l of H_2SO_4.
Assuming that the solubility product for the plant jarosite determined in section 2.2.2:

$$L = 0.00845 = [Fe^{3+}]^{0.927} * [NH_4^+]^{-0.59} * [H_2SO_4]^{2.13} \quad (73)$$

is valid also in this case, the equilibrium concentration of Fe^{3+} would only be about 4 and 2 g/l for reactions (70) and (71) in a solution with 1 g/l of NH_4^+ at 95 °C. If such results could be approached in a plant operation, it would be fully acceptable. These figures were very promising, and, consequently, a conceptual flowsheet, Fig. 52, was developed for how a process based on hydrolytic precipitation of the iron as jarosite could be performed [**XII**]. The leaching circuit would consist of the same steps as in a conventional Goethite process, except that the goethite precipitation is replaced by the hydrolytic precipitation of jarosite, where no calcine addition would be needed. In this flowsheet, the pre-neutralization of the reduced iron containing solution, 12, is done by recycling it through the neutral leach II step before it goes to the jarosite precipitation. This would save one process step, but a separate pre-neutralization step would, on the other hand, probably be easier to control.

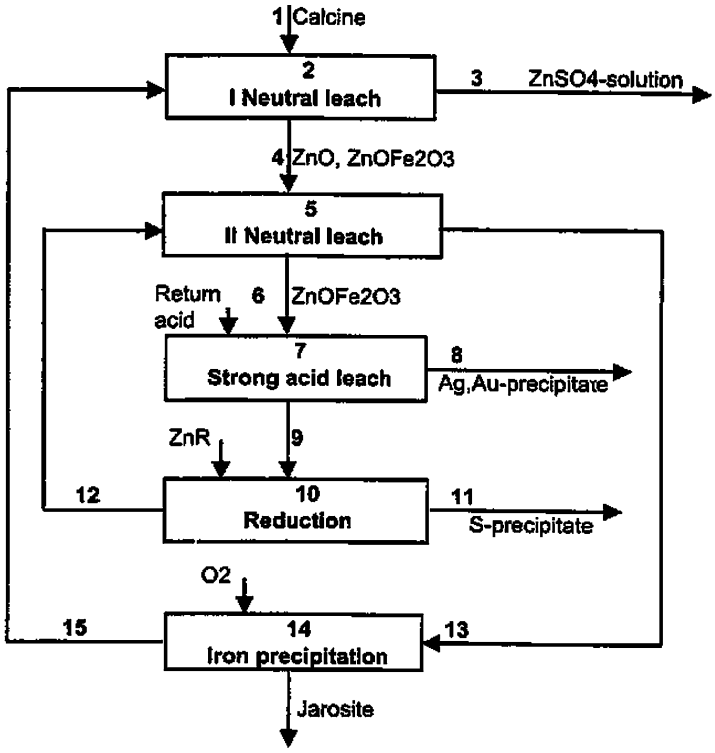

Fig. 46. Conceptual flowsheet for a "low contaminant jarosite" based on iron precipitation as jarosite from ferrous iron solution.

This flowsheet would, similarly to the process by Electrolytic Zinc of Australasia, provide:

- the High Acid Leach, HAL, residue would contain all Pb/Ag/Au entering the plant. This would improve the possibilities for a profitable recovery of these elements.
- very good filterability of the iron residue as the jarosite precipitation would take place at an acidity level; 5to 8 g/l of H_2SO_4, where no precipitation of hydroxides will take place. Also very minor quantities of SiO_2 would precipitate because practically all soluble SiO_2 would be precipitated in the pre-neutralization step, and, finally, be deported with the HAL residue.

If the S-precipitate, 11, is returned to the roaster, as is practiced in goethite operations, the only losses of Zn would be with the High acid leach, HAL, residue, 8, and the small quantity which will be incorporated in the jarosite crystal lattice. This would give an overall Zn recovery in the plant exceeding 99%, or 3 to 5% units above what is normally obtained in the Goethite Process. It would also be around 1% better than for a Conversion process. In addition the process will allow a high recovery of In, Ga and Ge to the solution from the

reduction step, (Fig. 52, step 12), as no metals are lost with a neutralizing calcine in the iron precipitation. These elements could then be recovered from the solution by a simple neutralization. These advantages would raise a possibility for recovery of all valuable elements up to the same level as in the Hematite Process.

All steps in the process, except for the jarosite precipitation, were known to be operating on industrial scale and, accordingly, experimental work for verification was needed only for this step. With the promising prospect for this process laboratory experiments were initiated.

5.2.2. Experimental

As the feed solution to the jarosite precipitation step would be rather constant with respect to Fe^{2+} ions, around 25 g/l in plant operation, the main variable parameters to investigate would be the influence of oxygen pressure, the seeding with jarosite and the NH_4^+ concentration level needed, which should be as low as possible to minimize the risk for jarosite formation in the other steps of the leach circuit.

Totally twenty-nine batch experiments were performed with synthetic solutions containing 100 g/l of Zn^{2+} and 25 g/l of Fe^{2+} with varying concentrations of NH_4^+, jarosite seed and oxygen pressure. To facilitate the oxidation of Fe^{2+} to Fe^{3+}, a concentration of 0.5 g/l of Cu^{2+} was also kept constant in all experiments. To vary the pressure of the oxidizing agents, i.e. air and O_2 gas, the experiments were conducted in an autoclave at about 95 to 100 °C.
The amount of jarosite seed was varied by transferring part, or all, of the precipitate from one batch to the following one. Samples were analyzed for H_2SO_4, NH_4^+, Fe^{2+} and total iron at certain intervals, whereas Fe^{3+} was calculated as the difference between the two analyzed iron species. The solids were followed by chemical analysis to clarify co-precipitation of Zn, Cu and F, which was added in a few batches. XRD was used for identification of the type of precipitate obtained.

Samples of the slurry were settled and the under-flow was filtered to give a picture of the filtration rate of the solid. This was determined with an in-house used filtration test in which the quantity of settled underflow should give a filter cake of around 5 mm thickness.

5.2.2.1 *Influence of acid concentration on hydrolytic precipitation of jarosite*

The first experiments were performed with "neutral" solutions (i.e. pH ≈3.5 to 4). This produced a precipitate consisting of a mix of jarosite and goethite, FeOOH, even with 5 g/l NH_4^+ and 100 g/l of jarosite seed added.
In the beginning the oxidation reaction can be written as

$$6Fe^{2+} + 6SO_4^{2-} + 1.5O_2 + 3H_2O \Rightarrow 6Fe^{3+} + 6SO_4^{2-} + 6OH^- \quad (74)$$

and it is faster than the jarosite precipitation, and at the high pH and Fe^{3+} concentrations goethite is formed:

$$6Fe^{2+} + 6SO_4^{2-} + 1.5O_2 + H_2O \Rightarrow 4Fe^{3+} + 6SO_4^{2-} + 2FeOOH \quad (75)$$

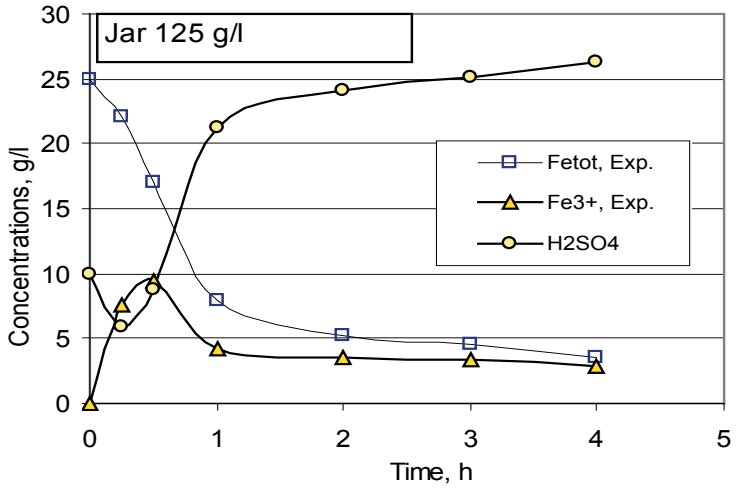

Fig. 47 Typical behaviour of total and ferric iron and acid in experiments on hydrolytic precipitation of jarosite.

Even though the H_2SO_4 concentration, through jarosite precipitation, increased to about 10 - 12 g/l at the end of the experiments, the initially formed iron oxy hydroxide, FeOOH, did not re-dissolve, at least not during an industrially relevant time. The filtration test gave very low rates, even down to 50 kg m^{-2} h^{-1} for these precipitates compared to around 200 kg m^{-2} h^{-1} for a normal plant jarosite. H_2SO_4 was then added to the feed solution to hinder the precipitation of FeOOH. With 5 g/l of acid, FeOOH was still detected, but, with 10 g/l only jarosite was found. The rest of the experiments were performed with an initial H_2SO_4 concentration of 10 g/l. At this stage, the filtering rate increased to more than 1000 kg m^{-2} h^{-1} for the pure jarosite.

Fig. 47 shows a typical example of the progress of experiments with 10 g/l of H_2SO_4 added to the start solution. In the 30 minutes the Fe^{3+} concentration increases up to a maximum, but has decreased after one hour down to below 5 g/l, where after it decreases very slowly. The H_2SO_4 concentration drops during the first 30 minutes of the run, to about 6 g/l at the lowest, due to the oxidation of iron (reactions 74, 75). This level is hence sufficient to prevent goethite precipitation at the prevailing conditions. Already after 1 to 2 h reaction time the Fe^{3+} level is sufficiently low, 3.5 to 3 g/l, to allow recycling the solution back to the neutral step.

5.2.2.2 Influence of NH_4^+ concentration

NH_4^+ concentration in the start solution was in the first experiments maintained at a level that should leave 2 to 3 g/l at the end, which was kept in the jarosite

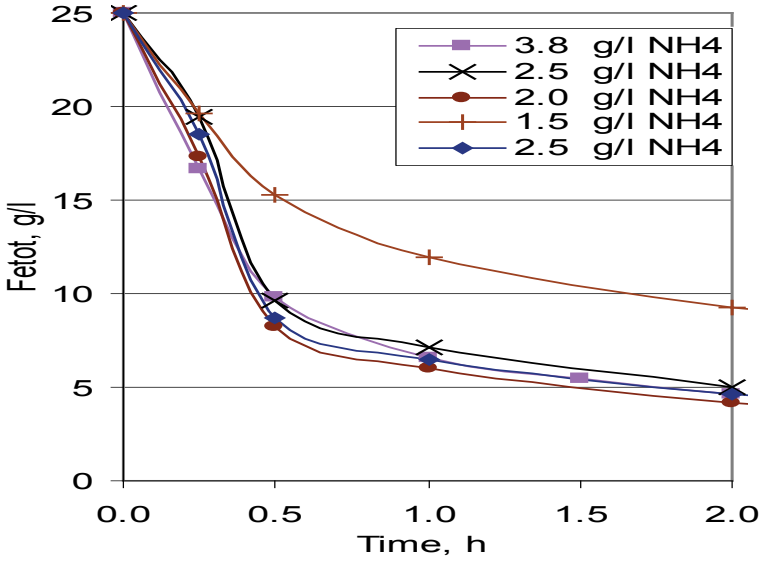

Fig. 48 influence of NH_4^+ on jarosite precipitation.

precipitation step in the plant. The initial concentration was decreased gradually from about 5 g/l in the first experiments down to 1.5 g/l, which is about 70% of the stoichiometric amount required to precipitate 20 g/l of iron as ammonium jarosite. Fig. 48 shows that the influence of NH_4^+ concentration is very minor on both the precipitation rate and degree even down to 2 g/l, and only at 1.5 g/l the influence is clearly visible. In the experiments with initially 2.5, 2 and 1.5 g/l of NH_4^+, the final NH_4^+ concentrations were about 0.9, 0.4 and 0.02 g/l. From these data and the amount of Fe precipitated it can be calculated that between 20 and 30% of the iron is precipitated as hydroniumjarosite without any clear dependence on the initial NH_4^+ concentration. The results show as well that it should be possible to maintain a

NH_4^+ level between 0.5 and 1 g/l in the final solution, which should hinder jarosite precipitation in the strong acid leach if concentrate is fed also to this step.

5.2.2.3 Influence of seeding

Fig. 49 shows that an increasing jarosite seed concentration and lower O_2 pressure are, as expected, lowering the Fe^{3+} concentration in the solution. This lowers the precipitation rate and the total iron increases. The influence of seeding on the Fe^{3+} concentration, which is the most critical, is, however, rather minor after the first hour and an initial seed concentration of 100 g/l would be fully satisfactory. After 4 h reaction time the Fe^{3+}, NH_4^+ and H_2SO_4 concentrations were about 2.5, 0.9 and 27 g/l respectively in the experiment with an initial concentration of 2.5 g/l of NH_4^+. At such NH_4^+ and H_2SO_4 concentrations, the above obtained solubility equation (section 2.2.2.) for the plant jarosite is

$$Fe = 0.00485*[NH_4^+]^{-0.59}*[H_2SO_4]^{2.13} \quad (76)$$

which gives a Fe^{3+} concentration of about 5.8 g/l. Hence the jarosite formed in this experiment is significantly more stable than the plant jarosite. This must strongly contribute to the very satisfactory iron precipitation, which was obtained in these experiments. Solubility determinations on this new jarosite were not done, but estimates were performed in connection with the mathematical modeling of the precipitation step shown below.

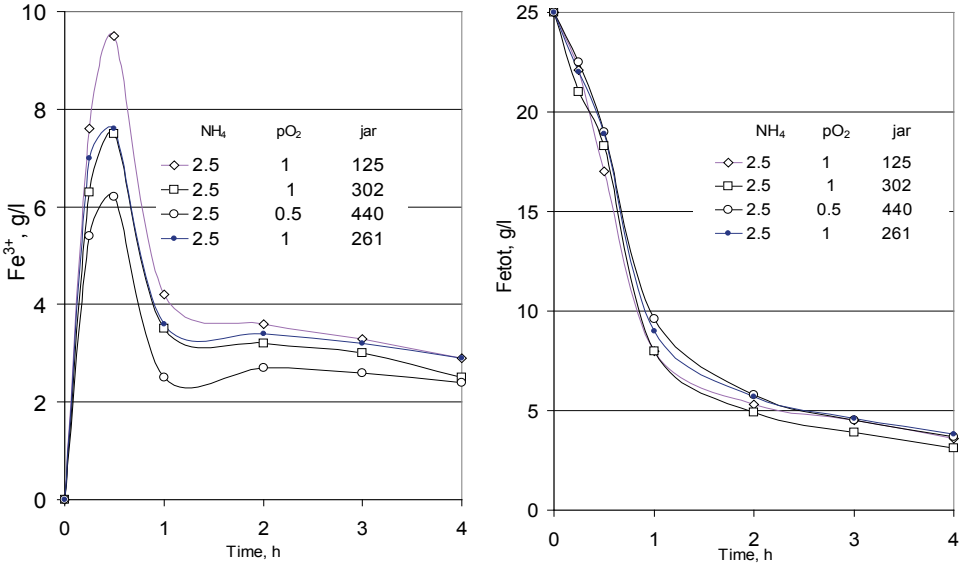

Fig. 49. Influence of seeding on ferric and total iron in hydrolytic precipitation of jarosite.

5.2.2.4 Influence of the oxygen pressure on the oxidation rate of Fe^{2+}

A power law model for the oxidation of Fe^{2+}, where only Fe^{2+} concentration was considered, was fitted to the results from three experiments carried out at 3, 1 and 0.5 bar O_2 pressure. This model did not give a good fit as seen in the left diagram in Fig. 56. The jarosite seed concentration in the experiments was, however, varied, and when also this was included in the parameters a very good fit was obtained, ($R^2 = 0.997$), as seen from the right diagram in Fig. 50.

The rate equations for the two models became:

$$-dFe^{2+}/dt = 0.461[Fe^{2+}]^{1.503}\ pO_2{}^{0.576} \quad (77)$$

$$-dFe^{2+}/dt = 0.318[Fe^{2+}]^{1.519} pO_2{}^{0.602}[jar]^{0.063} \quad (78)$$

The obtained influence of Fe^{2+} and pO_2 on the oxidation rate agrees well with the results obtained by Rönnholm in his Doctoral Thesis on oxidation of concentrated ferrous iron solutions [58]. As the jarosite does not take part in the oxidation reaction, the small influence could be caused by a mechanical effect.

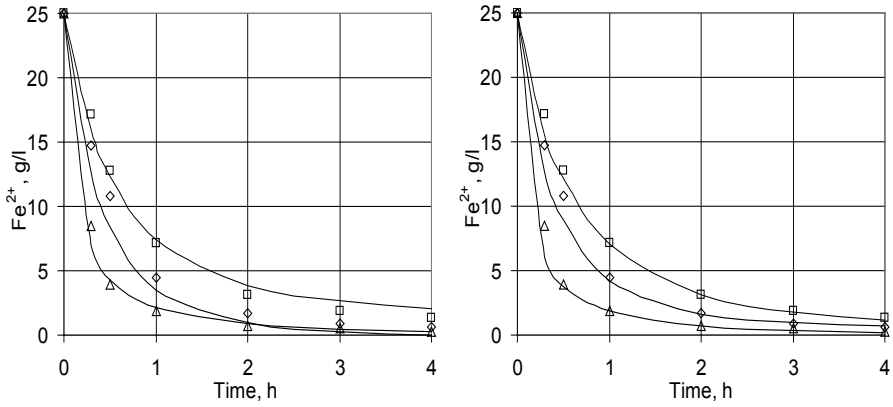

Fig. 50. Influence of oxygen pressure on the oxidation rate of ferrous iron.

5.2.2.5 Behavior of F-, Zn, Cu and Cd in the precipitation

20 and 100mg/l of fluoride (as NaF) were added in five of the experiments. Complete precipitation (< 1 mg/l) was achieved in 1 h in all cases. This is far above what have been experienced for co-precipitation in precipitation of jarosite from ferric iron solutions in the plant. Such a high degree of co-precipitations has neither been found reported in studies on fluoride removal in jarosite precipitation operations elsewhere. Zn was found to be in the 0.2 to 0.3% range in the jarosite, which is normally found also for co-precipitation from ferric iron solutions.

Cu was present in about 0.05% in the jarosite. With the concentrations of 100 and 0.5 g/l, respectively Zn^{2+} and Cu^{2+} in the solution the ratio of co-precipitation was about three times higher for Cu than for Zn.

Cd could be reduced to less than 5 ppm by washing. Dutrizac has also reported that Cd does not co-precipitate with jarosite [59].

5.2.3 Modeling of precipitation of jarosite from ferrous iron solution

In all experiments displayed in Fig. 51, the composition of the starting solutions was the same, Fe^{2+}, NH_4^+ and H_2SO_4 respective 25, 2.5 and 10 g/l. Only the quantity of seed and the oxygen pressure was varied as shown in the diagrams. It should thus be possible to determine the precipitation rate by these two variables. In Fig. 58 the fit of the Avrami model for total iron left in

solution as a function of time is shown, and the equation, (84), for residual iron, Fe_{tot}, show only a slight influence of oxygen pressure and seed content.

$$C_{Fetot} = 1 - \exp(-0.375 p_{O2}^{-0.183} C_{Jar}^{0.0032} t^{-0.628}) \quad (79)$$

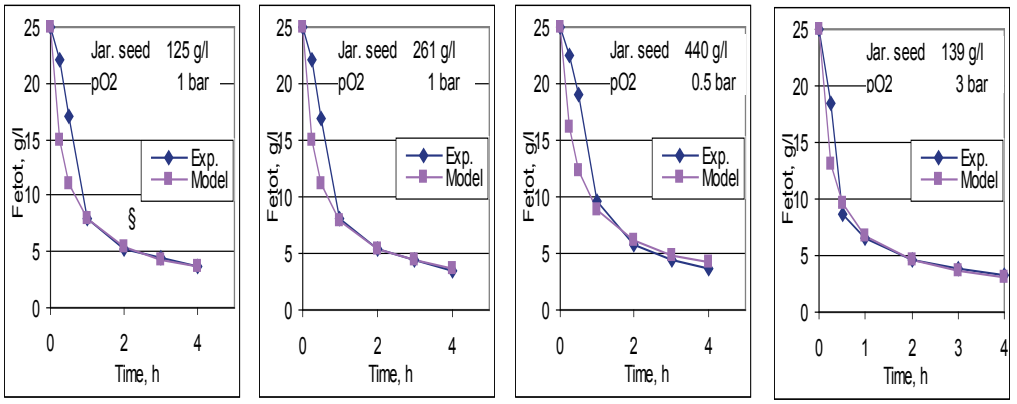

Fig. 51. Precipitation of jarosite from ferrous sulfate solution at different oxygen pressures and jarosite seed concentrations. Composition of initial solution 25, 2.5 and 10 g/l of respective Fe^{2+}, $NH_4^+$and H_2SO_4.

The discrepancy between the model and the experimental values in the beginning of the experiments was assumed to be caused by an incubation time. Fig. 51 reveals the calculated precipitation rates obtained from the experimental values and from the model. The model gives the maximum rate close to the maximum Fe^{3+}- and minimum H_2SO_4 concentrations, where the maximum should be, whereas in the experiment, it is at a later point with much lower Fe^{3+} and higher H_2SO_4 concentrations. Accordingly, only the results from 1 to 4 hours have been used in the calculation with the model.

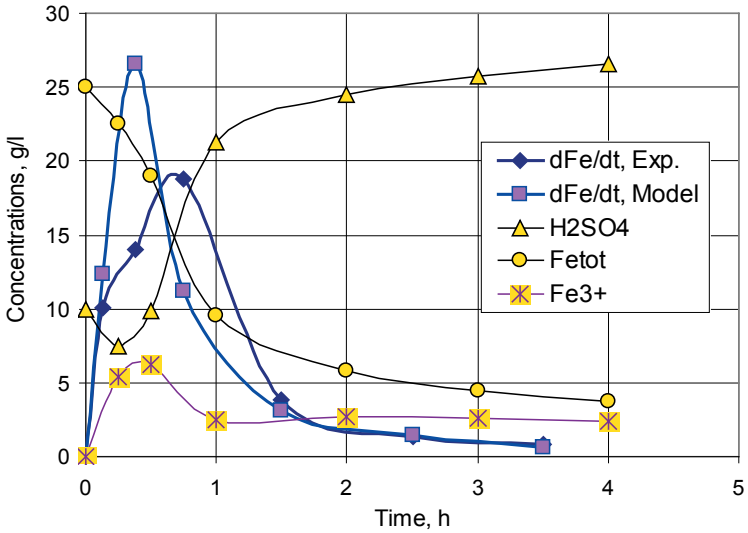

Fig. 52. Calculations of the dFe/dt from the values obtained experimentally and those calculated with the Avrami model.

Already the precipitation rates obtained from these experiments were fully acceptable as a basis for industrial application. In a continuous process, no addition of H_2SO_4 is needed, as the residence time in the first reactor can be selected in such a way that the amount of precipitated jarosite will be sufficient to keep the acid content at 5 to 10 g/l. The final acid concentration will then be 10 g/l lower than in the here described experiments and this will have a very positive effect on the precipitation rate and the final Fe^{3+} concentration. The residence time needed should then be well below four hours. This process has a clear economic advantage over the Goethite process, but also over the jarosite producing processes as summarized below:

- the recovery of all metals will increase as neutralizing calcine is not needed in the iron precipitation.
- if the sulfur residue is returned to the roaster, the Pb/Ag/Au residue will contain all what is fed to the process of these elements.
- in case of additional leaching of concentrate, most of these metals will end up in the residue from step 11 in Fig. 52 (S-precipitate). They can be separated from the sulfur/sulfide part by a simple flotation.
- the low end-concentration of NH_4^+, which according to the experiments on jarosite precipitation can be attained, will also eliminate jarosite formation in all leaching steps as iron can be kept in the ferrous state by feeding the concentrate to these steps. This will enhance both the formation of pure $PbSO_4$ leach residue and the recovery of In and Ga.
- at least compared to the normal jarosite precipitation (from Fe^{3+} solutions) this type of precipitation seem to be far more efficient for removing fluoride from the solution.

6. INDUSTRIAL ACHIEVEMENTS

A short summary of practical benefits regarding the plants competitiveness achieved from the development work is described section-wise below. The assessment of the benefits refers to the time of the introduction of the new technology. Even though other technologies have been improved, my feeling is that the presented technology in this thesis is still today on a highly competitive level.

6.1 Leaching of ferrite

The recovery of Zn was increased by about 4% by introducing the Conversion process in the equipment used for the two-step Jarosite process. Without additional costs, a 4% increased income, equal to about 8% savings in operating costs for the whole plant was obtained. Substantial investment, and some operating costs, was saved in the expansion project when compared to adoption of a "developed jarosite process" giving the same recovery, ≈ 98%, of zinc. Straightforward and simple process control gave a stable operation which produced a residue with good and stable filtering characteristics. Cutbacks in Zn production due to operational problems became very scarce.

6.2 Solution purification.

From an economic viewpoint, the most important is the savings in Zn powder consumption, which increased the capacity of the plant for saleable Zn by about 4%. With the cost structure of the plant, the impact on the economy was about the same as for the Conversion Process.

In the expansion project, the existing equipment was only rearranged, and new ones were needed only for the Cd removal. New buildings were not needed in the purification area. The control systems, (pH, Zn powder feeding), became more simple and reliable and reduced process interruptions and also decreased the problems with arsine in the plant. More stable and high-grade precipitates reduced filtration costs, saved investment in the Cd plant and reduced considerably the pollution with Cd and As at the Cu smelter.

6.3 Atmospheric leaching of concentrate.

The main improvements and savings originated from lower investment cost and simpler operation at atmospheric pressure compared with the competing autoclave leaching.
The proposed "clean jarosite process", based on hydrolytic precipitation of iron as jarosite from ferrous iron solutions, offers possibilities to obtain all Pb and

Ag fed to the Zn process into one leach residue. This will improve the possibility to have a feasible recovery process for these elements. Recovery of a major part of Ge, Ga and In will also be possible, and likewise the recovery of Zn, Cu and Cd would be improved to some degree, for Zn to over 99%.

6. 4 Various aspects

With the presented leaching processes, an extraction of Zn exceeding 99% can be reached, and the excess Zn powder consumption in the purification is less than 0.5 g/l (about 0.5% of Zn production). This implies that a further improvement on these figures through an improvement of the process chemistry will only have a very minor impact on the global competitiveness of the plant.

The greatest attribution to the competitiveness of the plant has, however, come from the two expansions of the plant (from 90000 to 275000 t/a of Zn). An objective assessment of the influence of the work presented here on the approval of these investments is difficult to make. It is, however, reasonable to suppose that positive decisions on financing are easier to make on a reliable and effective process, to which the presented improvements had an important contribution.

The importance of the research and development on sections 6.1 and 6.2 was assessed briefly in 1990. It showed that the savings from these process improvements exceeded the company's total expenditure for research on the zinc process by 5 to 6 times, and about 20 to 30 times the expenditure on the implemented processes only. The work demonstrates the success of a scientific approach in development of new technology.

Milestones in the history of the plant are listed in Table 11.

Table 11. Milestones of the Kokkola zinc plant.

Year	Technology		Capacity	Leach recovery	Zn powder	Capacity
	Added	Origin	t Zn/a	%	%	% of max[1)]
1969	Standard (Start up)	Purchased	90000	88	5	≈83-84
1971	Jarosite process	Purchased	90000	92		
1973	Conversion Process	Own	90000	96		
1974	Purification system	Own	170000	98	2.5 to 2	
1998	Concentrate leach	Own	270000	98	1.8	≈90

[1)] = capacity of the electrolysis at 100% current efficiency. Losses come from: current efficiency, Zn powder, dross in casting and loss from process disturbances.

7. CONCLUSIONS

This work summarizes how new knowledge on the chemistry involved in the jarosite-based leaching and "arsenic zinc dust" purification of the electrolytic zinc process was generated, and how new processes, based on this knowledge, were developed and implemented in the electrolytic zinc plant in Kokkola. By these processes the competitiveness of the plant was highly improved.

The Zn recovery in the leaching was increased from about 92 to 96% by replacing the two-step Jarosite Process with the one-step Conversion Process, in the same process equipment. When the plant capacity was expanded by about 100% the recovery could be raised to 98% only by adding new reactor volume with an investment cost far below the cost for commercially available technology giving the same result.

The Zn production of the plant was increased by about 3% through lower zinc powder consumption in the purification by adoption of new, separate, processes for Cu, Co and Cd removal. In addition, investment and operating costs were saved.

The acquired new information of thermodynamics and kinetics enabled development of stable processes with no demand for fast and frequent adjustments. Processes with simple and easy control gave stable operation with high plant availability

Except for the Cd-removal, all new processes could be run in the old equipment, which gave savings in investment costs in necessary plant expansions. Processes for atmospheric leaching of concentrates which favorably competed with the pressure leaching technology were developed.

Based on new data on the jarosite solubility, the leaching rate of zinc ferrite and precipitation rate of jarosite as a function of the acid concentration, the treatment of zinc ferrite could be performed in a one-step process. All ferrite fed to the leaching stage was then leached at high acid concentrations, which resulted in increased zinc extraction with a simpler process with less investment and some saving in operating cost.

Studies on the "hot arsenic zinc dust" process for Co removal revealed that Co, Ni and Cu probably precipitate as separate arsenides, CoAs, NiAs and Cu_3As, with no mixed arsenides being detected. This indicates that the three precipitation reactions are autocatalytic, and consequently, the volumetric precipitation rate should increase with increased concentration of precipitate. Experimental work along this line showed that the precipitation rate did

increase. In addition, also the selectivity, especially towards hydrogen evolution and cadmium precipitation, improved drastically. The results were substantially decreased zinc powder consumption and improved grade and value of the precipitate.

Fluidized bed principle was developed and adopted for the Cu removal. This saved Zn powder through formation of Cu_2O and reduced environmental risks at the copper smelter by reducing the content of Cd from about 1 to 2% down to less than 0.1% in the Cu-cake. The likewise fluidized bed based process for Cd removal produced a precipitate with 80% Cd and 10% Zn compared to 15 to 20 and 60% with conventional technology. This significantly saved Zn powder, and the coarse appearance of the precipitate reduced the tendency for re-dissolution and made it possible to replace the succeeding filtering step by hydro-cyclones. Due to the reduced solution flow, investment costs were saved in the Cd plant as well.

Atmospheric leaching of concentrate was studied as a possibility to develop a less costly technology than the commercially available autoclave leaching. Processes were developed both for Zn/Pb/Ag bulk concentrates, where profitable recovery of Pb and Ag is required, and normal Zn concentrates with minor value in these metals. Recovery of Pb/Ag meant production of a high grade, practically jarosite-free leach residue. The value of the leach residue from Zn concentrates could be kept low by buying concentrates with low Pb/Ag, and hence the grade of the residue was not important, and jarosite was therefore precipitated simultaneously with the leaching. The Fe^{3+} and NH_4^+ contents should then be as low and the H_2SO_4 content as high as possible for bulk concentrates and vice versa for Zn concentrates. Because the leaching rate of Zn concentrate is almost entirely dependent on the Fe^{3+} content, which again is dependent on the H_2SO_4 and NH_4^+ contents, meant for both processes a minimum acid concentration of about 20 g/l to keep the Fe^{3+} content at about 3 g/l. In the leaching of bulk concentrate, this is done by control of the oxidation potential so that most of the iron is kept in the Fe^{2+} state, whereas for Zn concentrate with simultaneous jarosite precipitation, through control of the acid concentration.

Studies made on the hydrolytic precipitation of jarosite by oxidizing ferrous iron solutions at atmospheric pressure revealed that this can well satisfy the need for iron removal from electrolytic zinc plants, especially if the leach solution is pre-neutralized. This will make it possible to have a process where all valuable metals, including In, Ga and Ge, can be recovered at high rates.
The work on the leaching stage brought the loss of insoluble zinc down to about 1%, and in the purification the loss in plant capacity, from over-stoichiometric Zn powder consumption, has been decreased to 0.5 - 0.8%.

These two figures represent the major cost items, and thus economic gain through further process-metallurgical improvements has been essentially limited. As the work has been mostly aimed at utilizing the equipment of the existing plant, a further development area could be in equipment design. Development of the process option with the iron precipitated from the ferrous state may also be a way to proceed, as this option makes additional recovery of all currently lost valuable elements possible.

The Avrami equation has given very good results in mathematical modeling of kinetics both in leaching and precipitation operations. The obtained semi-empirical kinetic rate models have shown to be very useful instruments in evaluation results of experimental series.

8. ABBREVIATIONS AND EXPLANATIONS

Extraction	Recovery to solution
HAL	High Acid Leach
NL	Neutral leach
OK	Outokumpu ltd
Recovery	Recovery to solution minus loss of water-soluble with residues.

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